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TRANSACTIONS

OF THE

AMERICAN CERAMIC SOCIETY

CONTAINING THE PAPERS AND DISCUSSIONS

OF THE

FIFTH ANNUAL MEETING

HELD AT

BOSTON, MASS.

FEB'Y 2-4, 1903

The Society is not, as an organization, responsible for the statements of fact or opinion expressed in its papers and discussions.

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RULES.

OBJECTS.

The objects of the American Ceramic Society are to promote the arts and sciences connected with Ceramics by means of meetings for social intercourse, for the reading and discussion of professional papers, and for the publication of professional literature.

MEMBERSHIP.

The Society shall consist of Honorary Members, Members and Associates.

Honorary Members must be persons of acknowledged professional eminence, and shall not exceed five in number.

Members shall be persons competent to fill responsible positions in Ceramics and have suitable qualifications.

Associates shall include persons interested in Ceramics and the allied arts.

Honorary Members shall be proposed by at least five Members, approved by the Council, and receive at least 90 per cent. of the votes cast by letter ballot at the annual meeting.

Members and Associates shall be proposed by at least three Members or Associates, approved by the Council, and receive at least 75 per cent. of the votes cast by letter ballot. A candidate for admission must make application on a form prepared by the Council which shall contain a written statement of his age, professional experience, and that he will, if elected, conform to the laws, rules, and requirements of the Society.

All Honorary Members, Members and Associates shall be equally entitled to the privileges of membership, except that only Members shall be entitled to hold office and to vote. Applicants for a change in grade of membership shall conform to the requirements of a new applicant.

Any person can be stricken from the membership of the Society on the request of five or more Members, on the recommendation of a majority of the Council, if he fails to resign on the advice of the Council. Such person, however, shall first be notified of the charges against him, and be given a reasonable time to appear before the Council, or present written defense, before final action is taken by the Council.

DUES.

Honorary Members shall be exempt from all dues.

The initiation fee of Members shall be ten dollars, and of Associates five dollars, which if not paid within six months after election, will render the election void.

The annual dues for Members will be fixed by the Council, but shall not exceed five dollars per year.

The annual dues for Associates will be fixed by the Council, but shall not exceed four dollars per year.

Any Member or Associate in arrears for over one year may be suspended from membership by the Council until such arrears are paid.

OFFICERS.

The affairs of the Society shall be managed by a Council, consisting of a President, Vice President, Secretary, Treasurer, and three Managers, who shall be elected from the members at the annual meeting, and hold office until the adjournment of the meeting at which their successors are elected.

The President, Vice President, Secretary and Treasurer shall be elected for one year, and the Managers for three years; and no President, Vice President, or Manager shall be eligible for immediate re-election to the same office.

The duties of all officers shall be such as usually appertain to their offices, or may be delegated to them by the Council or the Society; and the Council may at its discretion require bonds to be furnished by the Treasurer.

Vacancies in any office shall be filled by appointment by the Council, but the new incumbent shall not thereby be rendered ineligible to re-election at the next annual meeting to the same office. On the failure of any officers to execute his duties within a reasonable time, the Council, after duly warning such officer, may declare the office vacant, and appoint a new incumbent.

A majority of the Council shall constitute a quorum; but the Council shall be permitted to carry on such business as it may desire by letter.

ELECTIONS.

At the annual meeting, a nominating committee of five Members, not officers of the Society, shall be appointed, and this committee shall send the names of nominees to the Secretary at least 60 days before the annual meeting, who shall immediately forward the same to the Members. Any other five members may also present the names of any candidates to the Secretary, provided it is done at least 30 days before the annual meeting. The names of all candidates, provided their assent has been obtained, shall be placed on the ballot without distinction as to nomination by the regular or an independent nominating committee, which shall be mailed to every member, not in arrears, at least 20 days before the annual meeting.

The ballot shall be inclosed in an inner blank envelope, and the outer envelope shall be endorsed by the voter, and mailed to the Secretary for collection. The blank envelopes shall be opened by three Scrutineers appointed by the Chair at the annual meeting, who will report the result of the election. A plurality of the votes cast shall elect.

MEETINGS.

The annual meetings shall take place at such time and place as the Council may decide, at which time reports shall be made by the Council, Treasurer, and Scrutineers of election, and the accounts of the Treasurer, audited by a committee of three appointed by the Chair.

Other meetings may be held at such times and places during the year as the Council may decide, but at least 20 days' notice shall be given of such meetings.

Seven Members shall constitute a quorum at any regular meeting, and a majority shall rule, except where otherwise specified.

The order of business at the annual meeting shall be:—

1. Reading of Minutes of last meeting.
2. Reports of the Council and Treasurer of the Society.
3. Announcement of Election of Members.
4. Announcement of the Election of Officers.
5. Appointment of Nominating Committee.
6. Old Business.
7. New Business.
8. Reading of Papers.

PUBLICATIONS.

The Council shall act as a Publication Committee, and decide as to what to publish. The publications of the Society shall be sent to all Members and Associates not in arrears. The Secretary will furnish each author with reprints of his papers at cost price, provided due notice is given that reprints are desired.

The Society is not, as a body, responsible for the statements or opinions expressed in its publications.

PARLIAMENTARY STANDARD.

Roberts' "Rules of Order" shall be the parliamentary standard on all points not covered by these rules.

AMENDMENTS.

These rules may be amended at any regular meeting by a two-thirds vote of a letter ballot at the subsequent annual meeting provided a written notice of such proposed change is sent to each Member at least 30 days before said annual meeting. Said proposed amendments shall be printed on the ballot for officers and counted by the same Scrutineers.

PUBLICATIONS.

The publications of the Society are as follows:

DESCRIPTION OF VOLUME.	Price to Members.	Price to Others.
Vol. I. Transactions for 1899, 110 pages, bound in paper,	$0.50	$4.00
Vol. II. Transactions for 1900, 278 pages, bound in paper,	2.00	4.00
Vol. III. Transactions for 1901, 230 pages, bound in paper,	1.00	4.00
Vol. IV. Transactions for 1902, 300 pages, bound in paper,	1.50	4.00
Vol. V. Transactions for 1903, 420 pages, bound in paper,	2.00	4.00
Manual of Ceramic Calculation (contained in Vol. II as a part thereof,) 86 pages, bound in paper,	1.00	1.00
The Collected Writings of Dr. Hermann August Seger, Volume I. Contains (A) Treatises of a general scientific nature, (B) Essays relating to Brick and Terra Cotta, Earthenware and Stoneware, and Refractory Wares. Pages, 552. Bound cloth,	7.50	7.50
The Collected Writings of Dr. Hermann August Seger, Volume II. Contains (B) Essays on Whitewares and Porcelain. (C) Travels, Letters and Polemics. (D) Uncompleted works, and extracts from the archives of the Royal Porcelain Factory. Pages, 610 (est). Bound in cloth,	7.50	7.50

Every member or associate receives one copy of the Transactions free for each year for which he pays dues. He is entitled to purchase copies for the years antedating his connection with the Society at the costs indicated in the first column. All others can obtain copies at the prices listed in the second column by sending order, accompanied with check, to

STANLEY G. BURT,

Care of Rookwood Pottery Co.,

CINCINNATI, OHIO.

PREFACE.

The following pages constitute the record of the Society's fifth year of work. The meeting at Boston was the most largely attended of any yet held, in spite of the location being so far from the center of our geographical distribution. Also, the programme was longer, and more fully occupied than ever before. The trips and visits made by the Society added greatly to the value and enjoyment of the meeting.

The policy of publishing papers not yet read, or read by title only, has been continued and extended. Half of the present volume is of this sort, and some of the ablest papers are in this list. Also, many of those read were not discussed at the meeting for lack of time and lack of preparation of the members, and have been discussed in writing since.

The problem immediately before the Society is still much the same as one year ago. We need to diminish the time spent in listening to the reading of papers, and to increase the time spent in discussing those which we have had opportunity to read and study in advance. The first step in this direction was taken in the case of Mr. Fiske's paper this year. The results have encouraged the Council to make the following offer, viz.: Those papers sent in to the Secretary thirty days before a meeting will be printed and distributed in advance, to be used as a basis of prepared discussions. These discussions will be given the preference on the programme, other things being equal, over papers not printed in advance.

This step, it is confidently believed, will do much to strengthen the work of the society. The discussions of Mr. Fiske's paper, and also Mr. Hull's paper on Chrome Tin Pink may be taken as indications of what may be expected.

The work of the Society, as evidenced by the volume, shows a progressively broadening scope. Not only is the quantity greatly in excess of previous years, but also the variety of topics treated and the amount of new and independent research is equally increased. The field of the hydrous silicates especially has been greatly developed by the two important researches now published, and the fields of the slags and glasses have received attention in our literature for the first time, thus leaving no large field of silicate technology wholly untouched.

It is a pleasure to state that the general condition of the Society, judged by the cruder tests of increasing membership, broadening geographical range, and financial solvency, is most excellent.

EDWARD ORTON, JR.,
Secretary.

Columbus, O., July 20, 1903.

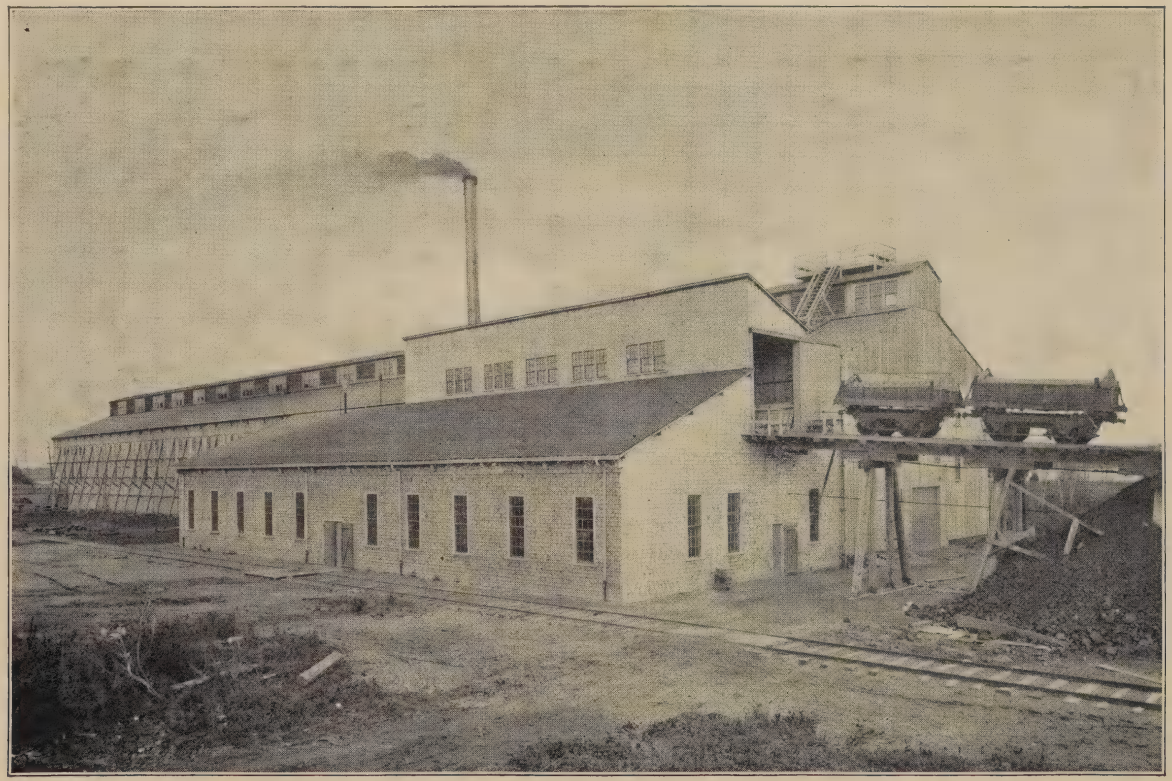


PLATE 1.—EXTERIOR VIEW OF FACTORY.

THE ELIMINATION OF HAND LABOR IN BRICK MAKING.

BY

J. PARKER B. FISKE, B. Sc., BOSTON, MASS.

All observing persons will agree that the manufacturing world has practically been revolutionized within the last quarter of a century by the use of labor-saving machinery. Hardly a class of manufacture exists that has not felt its magic touch, and with its aid the United States has become the foremost manufacturing country in the world. A manufacturer in nearly every industry who should return to the practice of even ten years ago in preference to that of today would invite failure and bankruptcy.

This is the age of machinery — automatic machinery, often with the most intricate mechanism, which works with marvelous speed and accuracy, and which accomplishes tasks far beyond the capability of the human hand, both in quality and quantity of product manufactured. As a result of such machinery, the cost of nearly all manufactured articles has been enormously reduced and the consumption by the people correspondingly increased.

It is the purpose of this paper to discuss the application of machinery to the art of brick making, with a view to the practical elimination of hand labor.

Much ingenious and useful brick machinery has already been invented and is in daily use in hundreds of plants; this is, however, largely confined to the preparation and handling of the clay and the forming of the soft bricks. This machinery has been perfected to such a point that little improvement is needed or can be expected in future, and the same remarks are doubtless true of the most modern types of drying and burning devices.

No successful attempt has been made, however, so far as I am aware, to eliminate the manual labor involved in handling the bricks from the brick machine through the

various processes of drying, burning, storing and delivery to the user, and inasmuch as this labor of handling constitutes a large part of the entire labor involved in the manufacture, comparatively little saving has been effected in the total labor cost.

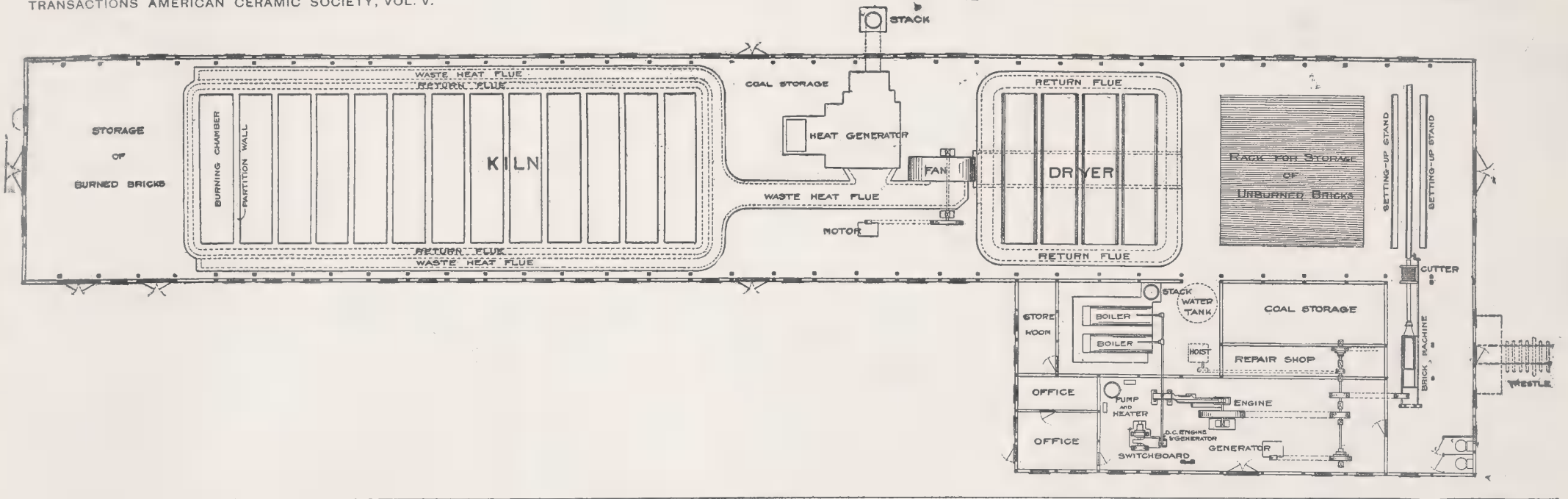
Certain improvements, such as the various car and truck systems, have come into use to a large extent, but these have been adopted mainly because of their convenience and adaptability to the artificial drier rather than as labor-saving devices pure and simple. These devices must still be propelled over long distances by man power and the bricks, even under the most favorable conditions, must undergo repeated handlings in setting and emptying the kilns and in loading the delivery cars or wagons.

The number of hand operations in modern brick making varies greatly, depending upon the process, whether molded by the "soft mud" or the "stiff mud" machines, whether dried on the open yard in racks or in artificial driers, and whether burned in up draft, down draft or continuous kilns. It is fair to say, however, that an average of all plants would show from 12 to 15 hand or man power operations, from the time the bricks are molded until they are loaded on the delivery wagons.

When the value per ton of the finished product is taken into account, this amount of hand labor appears excessive; thus a ton of common bricks is worth on the average say two and a half dollars on the wagon or cars at the plant, while a ton of steel rails at twenty dollars has excited the wonder of the whole world. Such a low value should involve a minimum of hand labor per unit of weight, yet it is doubtless true that no finished product in the world involves so much.

In short, an excessive proportion of the entire cost of brick making today is in the labor item, and our only hope of substantial reduction lies in the minimizing of this hand labor.

The prime necessity for the successful use of automatic machinery in any art is that every unit of manufacture shall be subjected to precisely the same treatment, and this



GROUND PLAN OF PLANT. SCALE ABOUT 30 FT. TO INCH.

STORAGE
OF
BURNED BRICK

condition obtains to an ideal extent in the art of brick making. Thus, particularly in the case of common bricks, every piece is molded or pressed exactly like its mates, and is subjected to the same drying and burning heats and, theoretically, when finished should be of exactly the same size, shape and texture.

However, a careful study of this problem will, I think, convince anyone that no great improvement can be made in the "summer brickyard;" that is, one in which the drying is done by sun and wind, as these elements are intermittent in their action and are so uncertain at best that manufacturing can be conducted not over one-third of the total number of working days in the year. It is also important for the profitable use of labor-saving machinery that it shall be worked systematically and continuously in order that it may have an opportunity to earn a fair interest on its first cost, which is necessarily high. To make any radical improvements, therefore, the "open yard" idea must be abandoned and a permanent, substantial construction must be adopted, with the best possible form of brick molding machinery, artificial driers and fuel saving kilns, specially constructed to suit the new conditions involved in the use of automatic handling machinery, the whole plant representing a comprehensive scheme complete in all its arrangements, so that the raw material may enter at one end, proceed systematically through the various processes and emerge a finished product at the other, practically without hand labor.

Having perfected such a system and put it into successful operation at the works of The Fiske Brick Co., at Dover Point, N. H., I take pleasure in presenting a description of it to this society.

Plate 1 shows a photograph of the exterior of the main building, with monitor roof, 367 feet long and 60 feet wide, and the auxiliary building being 115 feet long and 50 feet wide.

Plate 2 is a plan view of the plant thus far erected, and shows:

Power Plant, consisting of two tubular boilers, pumps and feed water heater, a 200 H. P. Corliss engine, 50 kilowatt

belted dynamo, 50 kilowatt direct connected engine and dynamo as a spare unit, switchboard, shafting, etc.

Brick Machinery, consisting of a Chambers disintegrator and a Freese combined pugmill and auger machine for making stiff mud bricks, with an automatic cutter and an off-bearing belt extending nearly across the main building.

Setting-Up Stands for the reception of the green bricks as they are taken from the belt.

Drying Arrangements, consisting of a Crown Heat Generator, a twelve-foot Sturtevant fan and four drying chambers of special construction, as described later.

Kiln, consisting of thirteen chambers arranged in one battery for burning by the continuous or regenerative principle.

Plate 3 is a bird's-eye interior view looking north, and shows the storage rack and drier in the foreground.

The clay is drawn up an inclined trestle in side dumping cars, each of five yards capacity, and is dumped into a hopper at the disintegrator. The material proceeds through the disintegrator, brick machine and cutter, and the green bricks pass out into the main building on the off-bearing belt, all in the usual manner.

At this point in the manufacture the special handling machinery begins its work, the process thus far being an entirely standard one.

Careful consideration of the conditions necessary for the drying and burning of bricks has convinced me that the successful handling machinery must handle the bricks in large masses rather than one by one, as is done by labor saving machinery in other arts, and I consequently introduce at this point in the manufacture what I term the "unit stack" idea, which I believe to be entirely novel in brick making.

The unit stack consists of a pile of bricks built up, as they issue from the molding or pressing machine, in such relative position, brick to brick, that they can be dried, burned and loaded on the delivery car or wagon without rearrangement, the entire stack being lifted as a unit, transported and deposited by suitable machinery, first into

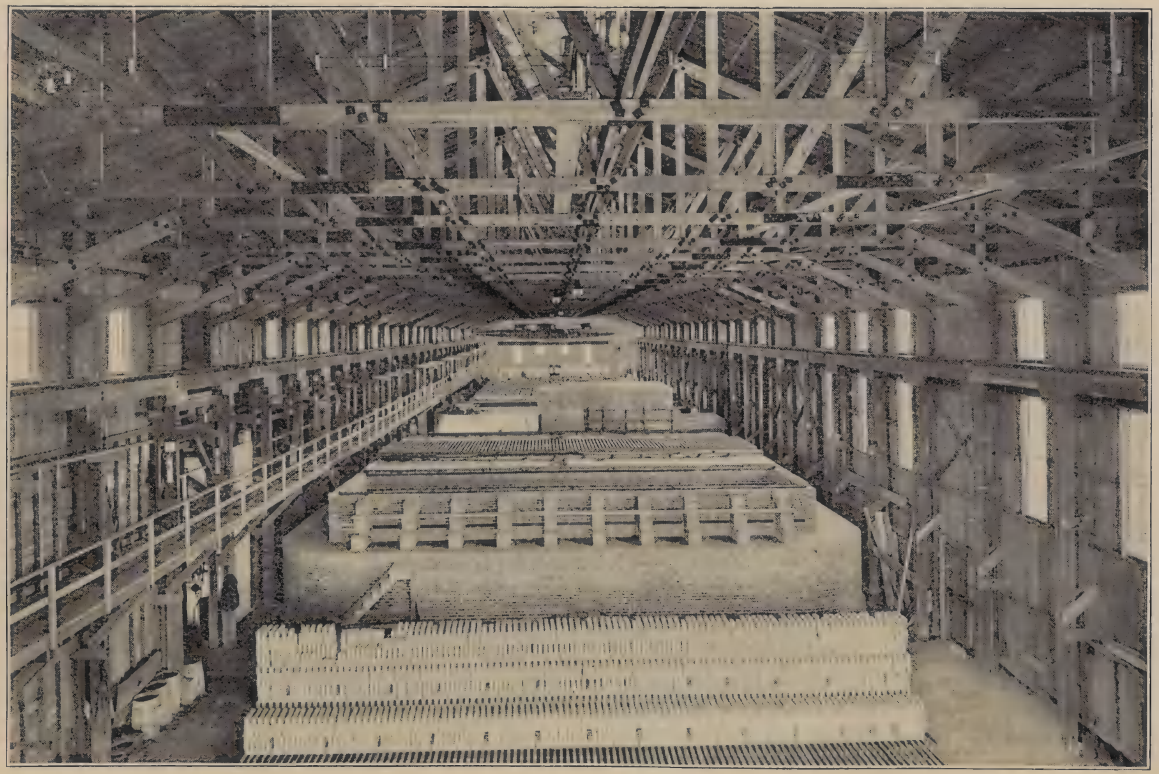


PLATE 3.—BIRDS EYE VIEW OF INTERIOR OF MAIN BUILDING, SHOWING STORAGE RACK FOR DRIED BRICK IN THE FOREGROUND.

the drier, then into the kiln, and finally into the stockyard or delivery wagon. The original stacking can be done automatically, layer upon layer, by machinery, or can be done by hand as in the plant under discussion.

The unit stack system creates a distinct advance in the art, as it eliminates all manual handling after the bricks are once stacked, banishes from the brick factory all tip carts, trucks, wheel-barrows, drier cars, tracks, transfer cars and turn-tables, dispenses with kiln "setters" and "emptiers," and reduces the entire force of employes, beyond the brick machinery gang proper, to a mere handful of men.

In order to place the bricks in unit stack formation, a rack called a "setting-up stand" is permanently located on each side of the off-bearing belt, and at a suitable distance therefrom to accommodate the stackers.

Plate 4 shows the sitting-up stands, constructed with 105 heavy horizontal bars of hard pine, mounted at a convenient height for the stacking of the bricks, these bars being spaced apart so as to support each lower brick at its two ends and in the middle, leaving two clear spaces about $1\frac{1}{2}$ inches wide under each bottom row. The bricks may be set five over two, six over two, or in any manner required for their proper drying and burning, exactly as is done in the usual plant, and no more care is required than in setting bricks in an ordinary kiln. For these reasons a very wide variety of clays can be handled by this system, as any style of setting may be adopted which is found necessary to suit the peculiarities of the clay in question.

The stand is about 39 feet long by 20 inches wide, and holds about 1,500 bricks when stacked five over two (that is, five headers over two stretchers) and six courses high. At the back of the stand are vertical guide bars, also of hard pine, to insure a perfectly vertical stack and to guide the stackers in setting the top row of bricks, which must be spaced exactly to correspond with the horizontal bars, as will be seen later.

As soon as the first stack is completed, the stackers commence placing the bricks on the opposite stand, the first stack being soon removed by the handling machinery

thus leaving the first stand empty and ready for another stack. Thus all waiting for empty cars or trucks, as is common in many brick plants, is eliminated, and the brick machine is free to run without interruption. Plate 4 shows one stand filled and the other partially filled.

The handling machinery consists of an overhead electric traveling crane and a special carrier called a "brick lift."

By reference to Plate 5 it will be seen that the crane travels on tracks supported on an elevated runway near the eaves of the main building, and that it spans this building completely and travels its entire length. The crane is driven along the overhead tracks by an electric motor called the "travel motor," located midway on the crane girder and shown in the cut, and the hoisting and lowering of the load is effected by the "hoist-motor," located on top; each motor is controlled independently by a lever in the operator's cage. The hoisting is done by four vertical chains and four winding drums driven in unison by the main shaft from the hoisting motor.

The brick lift consists of two main lifting beams properly braced together to form a girder; to this girder are attached 104 lifting fingers accurately spaced apart to correspond to the spaces between the bars of the setting-up stand, so that the whole forms a rigid structure. The four vertical chains already mentioned are attached to four lifting eyes on the lifting beams, thereby securing the utmost stability of the loaded lift, tipping in any direction being impossible and swaying and twisting being reduced to a minimum.

To engage and transport a load of bricks, the lift is brought by the crane in front of the setting-up stand, lowered until the fingers are at the proper level, the crane moved forward until the horizontal members of the fingers are run into the spaces between the bars of the stand and underneath the lower layer of bricks. Plate 6 shows the fingers in the act of entering these spaces. The lift with the entire load of bricks is then raised clear of the stand by the hoisting motor, and is carried by the crane to the drier as a unit.

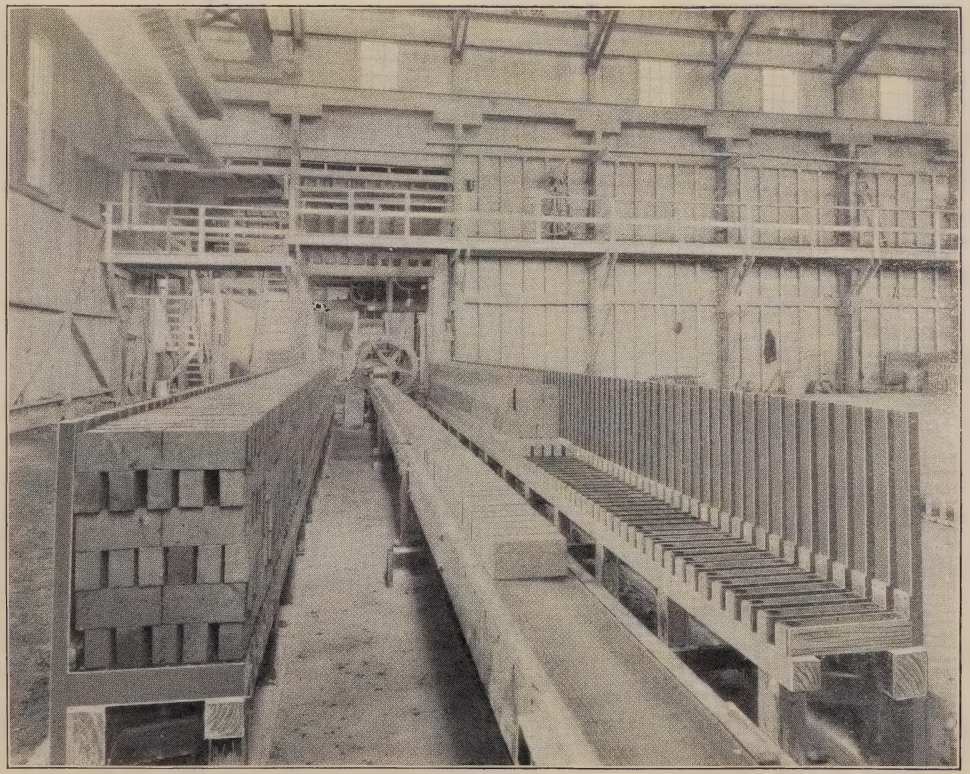


PLATE 4.—SETTING-UP-STANDS, ONE FILLED WITH SOFT BRICKS AND ONE PARTLY FILLED; THE OFFBEARING BELT BEING BETWEEN THEM.

By reference to Plate 7, it will be seen that each brick of the bottom layer is supported on two fingers of the lift, hence there is perfect stability of the load and it is impossible for it to twist or topple over. Repeated trials with the most violent movements of the crane that were possible have failed to dislodge a single brick from its load.

The crane operator is located in a cage at one end of the crane, as shown in Plate 5, and at all times has an uninterrupted view of the runway and of his work below.

It will be noted that this operator, with one helper on the brick lift, can handle as many bricks at a time as 15 to 20 men with wheelbarrows, and that the speed of travel along the tracks is faster than a man can comfortably walk.

Handling the unit stack during the remainder of the process is accomplished by the use of racks in the drier, kiln and store room, each constructed with horizontal members accurately spaced for the reception of the bricks as in the case of the setting-up stand and provided with spaces between its members to correspond to the fingers of the lift. Thus in the drier these racks are of steel I beams, in the kiln they are of bricks to withstand the heat necessary for burning the ware, and in the store room they are of either steel or wood.

The drier shown in section in Plates 8 and 9 is of brick and steel construction, is absolutely fireproof and is novel throughout. It is divided into four chambers by permanent partition walls, each chamber being provided with a cover removable in one piece; these covers are constructed of I beams with an upper and lower covering of sheet iron, thereby providing a dead air space of about 4 inches. Plate 10 shows one of these chambers with the cover removed, two stacks of soft bricks having been placed in the chamber.

In the bottom of each chamber is a fixed rack of I beams constructed as already described; the stacks of bricks are brought from the setting-up table and deposited successively upon this rack, the brick lift being lowered through the rack to deposit the bricks, and being backed out and raised from the rack each time after so depositing them.

As the soft bricks will not bear the weight of superimposed loads, each chamber is provided also with two removable racks, which are supported by horizontal channel beams built into partition walls separating the chamber. Each removable rack is built of I beams like the fixed rack below it, and each holds four stacks of bricks, thus making the capacity of each chamber 12 stacks, or about 18,000 bricks.

The arrangement of the covers and the racks with their loads of bricks is clearly shown in Plates 8 and 9.

The method of handling the removable racks is shown in Plates 11 and 12. Each rack is provided on its under side with two flat iron bars running lengthwise and equidistant from the center line of the rack. The fingers of the brick lift are dropped below the level of these bars and are then run under them so that the rack can then be lifted and transported, the bearing on the two bars preventing the rack from tipping or twisting.

The covers are provided with latticed lifting beams attached to the tops so that the fingers of the lift can be run under them for the purpose of handling the covers from one chamber to another. A cover is generally removed from a chamber of dried bricks and placed upon a chamber just filled with bricks to be dried. Each cover, when in position, is supported by channel irons on the top of the partition walls, as shown in Plates 8 and 10, these channels being filled with sand; a downwardly projecting lip on the cover imbeds itself in this sand when the cover is placed in position, thereby automatically sealing the chamber.

Hot air is forced through the bricks by a powerful fan driven by an electric motor, the air passing through three chambers in succession, as shown in Plate 9. Inasmuch as the bricks can not be progressed through successively hotter and hotter zones, as in the case of the tunnel drier, the same results are obtained by progressing the zone of maximum heat through the bricks. Thus the air being heated by a suitable device, in this case by a Crown Heat Generator, it is forced into a circular tunnel running lengthwise of the building and passing under the center of each cham-

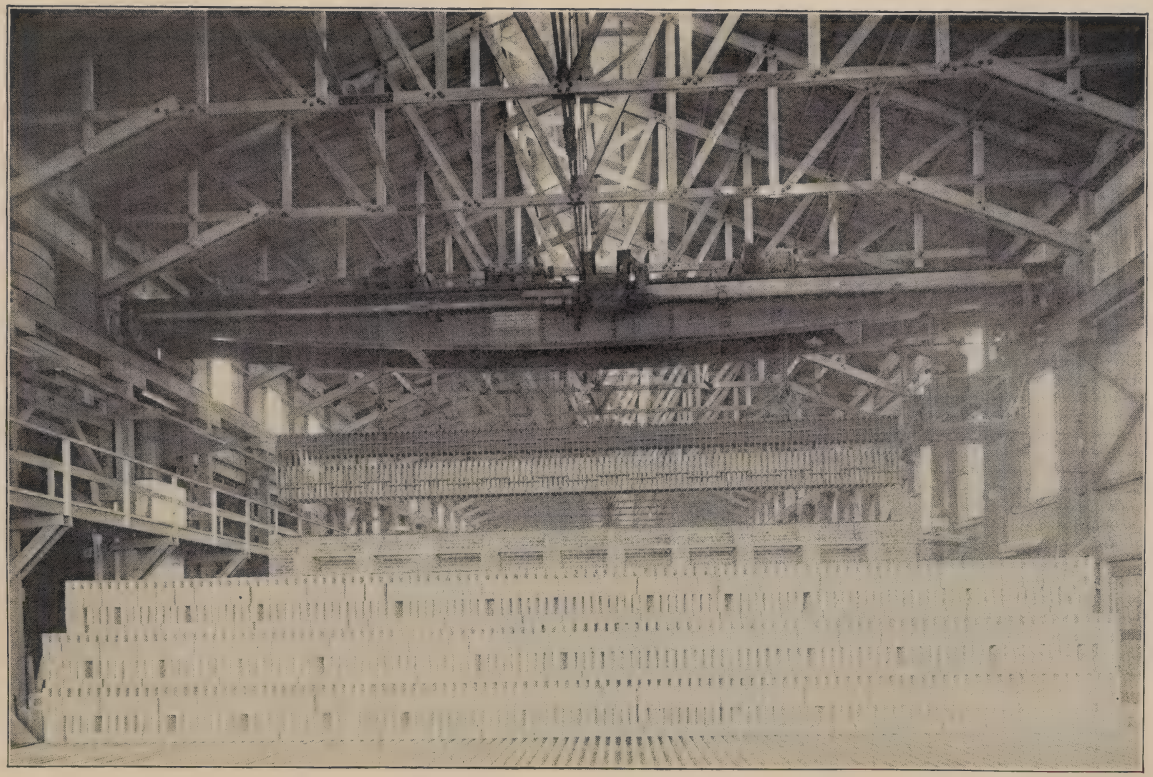


PLATE 5.—SHOWING CRANE TRAVELLING ON ELEVATED RUNWAY AND CARRYING A STACK OF SOFT BRICK TO THE DRYER. DRIED BRICKS IN STORAGE IN THE FOREGROUND.

ber, as shown in Plates 8 and 9. On each side of this tunnel and under each chamber is a large opening, closed by a curved hanging damper controlled by a chain from the outside of the drier. This opening admits just the proper amount of air to a distributing compartment located beneath the lower brick rack and provided with a sloping bottom to insure a proper flow of air into all parts of the drying chamber. The curved dampers being closed under all the chambers except the one of nearly dried bricks, the air passes from the tunnel into the distributing compartment, and thence upward through the bricks.

In order to facilitate the proper circulation, a wide space is left between the bricks at one side of the chamber and the partition wall, this space being insured by the room necessary for backing out the brick lift after depositing its last load on each rack. In the case of the lower rack, a wide sheet iron floor is attached to the lower side of the rack, underneath that portion covered by the bricks, in order to force all the air first into the clearance space and up to the cover, and thence downward and at more or less of an angle through the bricks to openings or wickets in the base of the opposite partition wall, and thence into the next chamber. To prevent the air from passing directly through the lower tier of bricks to the wickets, canvas baffle curtains are hung from the bottom of the two movable racks, thereby forcing the air up, over and then downward through the bricks. The wickets are closed by vertical sliding dampers, controlled by chains passing upward through 2-inch pipes imbedded in the partition walls.

The hot air is first admitted to a chamber of nearly dried bricks and passes thence to a partially dried chamber, thence to a chamber freshly filled and finally into an open chamber just being filled. As soon as the first chamber has been thoroughly dried and the last chamber has been filled, the cover of chamber No. 1 is removed, and is placed in position on No. 4, the hot air is shut off from the No. 1 and admitted directly to No. 2, which by this time has become sufficiently heated and dried to prevent checking of the ware. Chamber No. 1 is now ready to have its brick re-

moved to the kiln for burning. Chamber No. 4 is connected with Chamber No. 1 by return flues, located on either side of the drier in order that the chambers may operate in rotation without any interruption, as in the case of the continuous burning kiln.

Thus the zone of maximum heat is progressed from chamber to chamber, the nearly dried brick receiving the maximum heat and the green bricks being subjected to warm moist air as in the most approved types of progressive artificial driers.

The bricks are carried from the drier to the kiln by the crane and brick lift, and are there deposited, each chamber (holding about 18,000 bricks) having a removable crown, so as to leave the entire top open. The bottom of the kiln, or that portion covered by bricks to be burned, is provided with a special fire brick floor with separated ribs, corresponding in spacing to the fingers of the brick lift, so that the stack of dried bricks is deposited without difficulty and the lift withdrawn, as in the case of the drier, each brick of the lower layer being supported by the ribs of the floor at its two ends and in the middle. Plate 13 shows one kiln dried brick, and Plate 14, taken during the construction of the kiln and before the partition walls were built, shows the brick lift in the act of depositing a load of bricks on the ribs forming the special kiln bottom.

After the four stacks of bricks forming the lower tier have thus been placed in position in the kiln, other successive stacks have been placed upon them, the fingers of the lift passing down into the spaces of the upper row of bricks of the tier below. It will be noted that the upper row of bricks of each stack is spaced especially wide apart to permit this operation, as has already been described.

The setting consists of three tiers of four stacks each. After placing the last stack in position the empty lift is backed out into the "combustion space," and is then withdrawn from the kiln. In reverse manner, the lift enters the kiln when the bricks have been burned and cooled and removes one load after another to the point of shipping or storage.

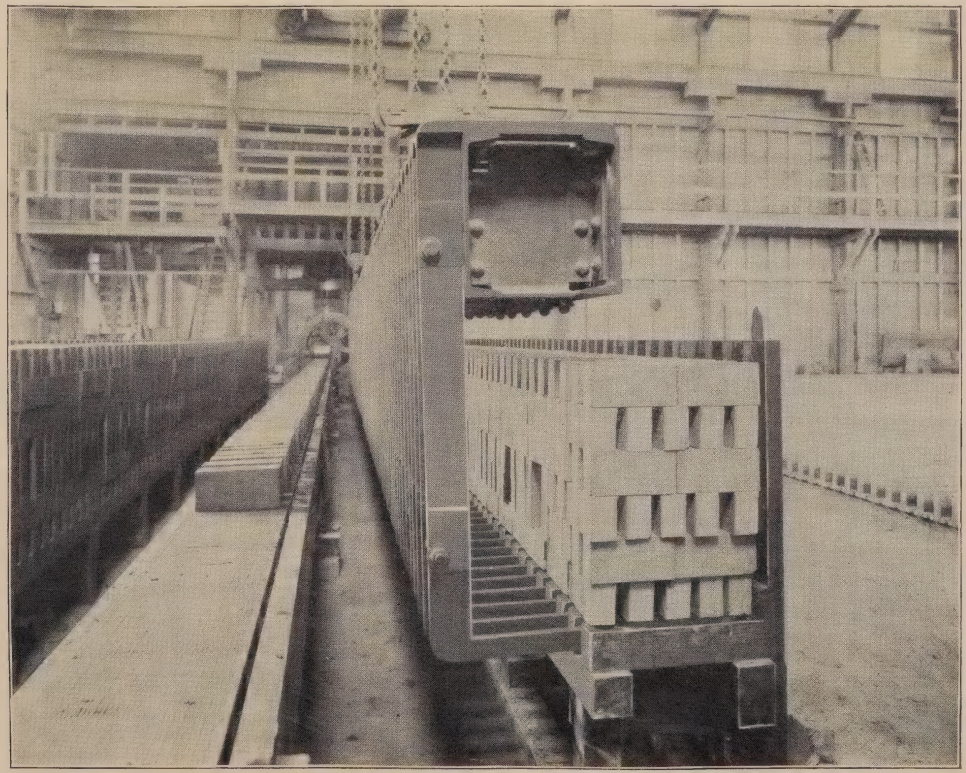


PLATE 6.- SHOWING THE FINGERS OF THE BRICK LEFT IN THE ACT OF ENTERING SPACES OF THE RACK, PREPARATORP TC LIFTING THE BRICK.

Plate 15 shows a kiln chamber filled with bricks ready for the reception of the portable crown.

The kiln operates on the "semi-continuous" principle, and is built with permanent transverse partitions, dividing it into chambers; the fires are fed with coal through holes in the crown and are supplied with hot air from the cooling chambers behind, the air entering the burning chamber through the "wickets" in the base of the partition wall; the waste heat of the burning chamber passes forward in a similar manner to heat up the green bricks in advance of the fires. Thus the utmost economy of fuel is secured.

Many novel features are to be noted in the construction and operation of the kiln under discussion.

The chambers are unusually low and narrow, which enables them to be fired largely from one side and to produce a very uniform burn.

The open space above mentioned acts not only as a combustion chamber, but provides an entrance and exit for the brick lift to the chamber when the latter is filled with bricks.

The removable crowns for the kiln chambers are constructed of fire clay blocks and cast iron hollow beams of special shape and section. These beams are placed about 18 inches apart by separating bolts and span the kiln chamber from one partition wall to the next, the ends resting on special cast iron channel irons anchored along the top of the partitions. The beams support heavy blocks, made of high grade fire clay mixed with sawdust to give porosity, the soffits of the beams being amply protected by fire clay key pieces.

The crown is sealed around the edge with soft bricks and sand and gives a construction of great superiority over the ordinary mason work arch. No lateral thrust of any kind on the side walls or partition walls is produced as the crown expands and contracts, the iron beams simply sliding on the channel iron supports. Moreover, repairs may be made to a crown by removing one or more fire clay blocks without tearing down the whole crown, and without interrupting the operation of the kiln, as is often

the case in ordinary fire brick construction. The crowns are lifted, transported and deposited by the crane and the brick lift, which engages a heavy latticed lifting girder attached to each iron beam of the crown. This construction provides a liberal amount of flexibility and secures a satisfactory seating of each beam on the wall without undue straining of the fireproofing materials. The construction of the crowns and the manner of lifting them are shown in Plate 16.

As all filling and emptying of the chambers are done through the top, the kiln is built with thick, permanent and unbroken side walls, all arched doorways being omitted. Thus the necessity of continually bricking up and tearing down the doors, as in other kilns, and the usual complement of soft burned bricks near the doorways are obviated. Moreover, as the side walls are unbroken from end to end, it is possible to build the kiln with all flues in the walls, thereby eliminating the underground flue absolutely. As is well known, underground flues are often cold and damp and are a source of great irregularity of draft, particularily in a continuous kiln, where the temperature of the waste gases is very low.

The draft for burning is produced by an exhaust fan driven by an electric motor, the whole being mounted on a portable cover, constructed of I beams and sheet iron covering, as in the case of the drier covers. A suitable iron pipe connects the inlet of the fan with holes through the cover at the proper points. The draft cover is transported by the crane and brick lift, which engages a lifting beam, as will be seen by reference to Plate 17. The draft cover is deposited over a kiln chamber a suitable distance ahead of the fire, and is advanced from time to time as the fire progresses. Thus the source of draft is always at a fixed distance from the fire, is direct, positive and uniform, and at once effectually overcomes all the difficulties experienced with natural draft.

The kiln is built in a straight line instead of in the usual oval shape, in order to bring all the chambers properly within the range of the overhead crane, and it may be

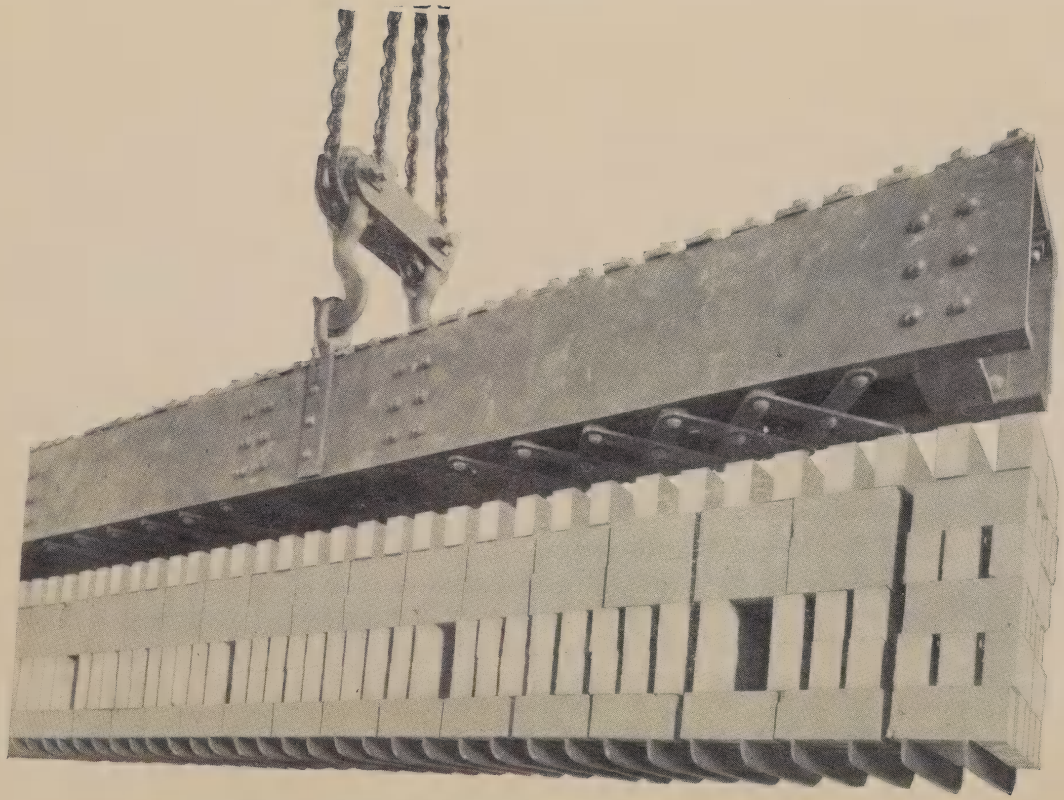


PLATE 7.—BRICK LIFT SUPPORTING A "UNIT STACK" OF BRICKS, SHOWING ONE END ONLY.

constructed on the semi-continuous principle, in which the fire is started at one end, traverses the length of the kiln and then dies out, or by the use of "return flues" connecting the two ends of the kiln, heat from the last chamber may be carried to the starting end for water smoking purposes, as in the case of the original continuous kiln. The latter arrangement is used in the Dover Point plant.

The improved continuous kiln not only saves two-thirds of the fuel and a large part of the labor of the up-draft wood burning kiln, but produces bricks of far more uniform color with practically no cracking, breakage or other loss.

The coal for firing the kiln is brought by the crane and brick lift, from the storage bin in long iron boxes, which are deposited on top of the kiln adjacent to the proper feed holes. These boxes are moved along from chamber to chamber as the fire progresses. Thus the wheeling of coal is minimized and no coal is wasted by being scattered over the top of the kiln. The ashes are taken out of the kiln by a similar box, which is lowered into the chamber after the bricks are removed.

When a chamber of burned bricks has become sufficiently cooled for removal to the stock pile, the crown is lifted by the crane and brick lift and deposited over a chamber just filled with dried brick. The brick lift is then lowered into the combustion space to a proper level, the fingers are run under the stacks of burned bricks, which are lifted and transported one by one to any desired point for assorting, storage and shipment. In plants making common bricks only the bricks may be deposited upon an automatic loading machine, consisting of an endless belt with separated slats or bars for receiving the bricks as in the case of the drier racks, this belt conveying the bricks and dumping them into the delivery wagon, thus reducing the entire hand labor on the plant to the single operation of stacking the soft bricks at the setting-up stands. Each unit stack will fill an ordinary delivery wagon. The same device may be used to load railway cars.

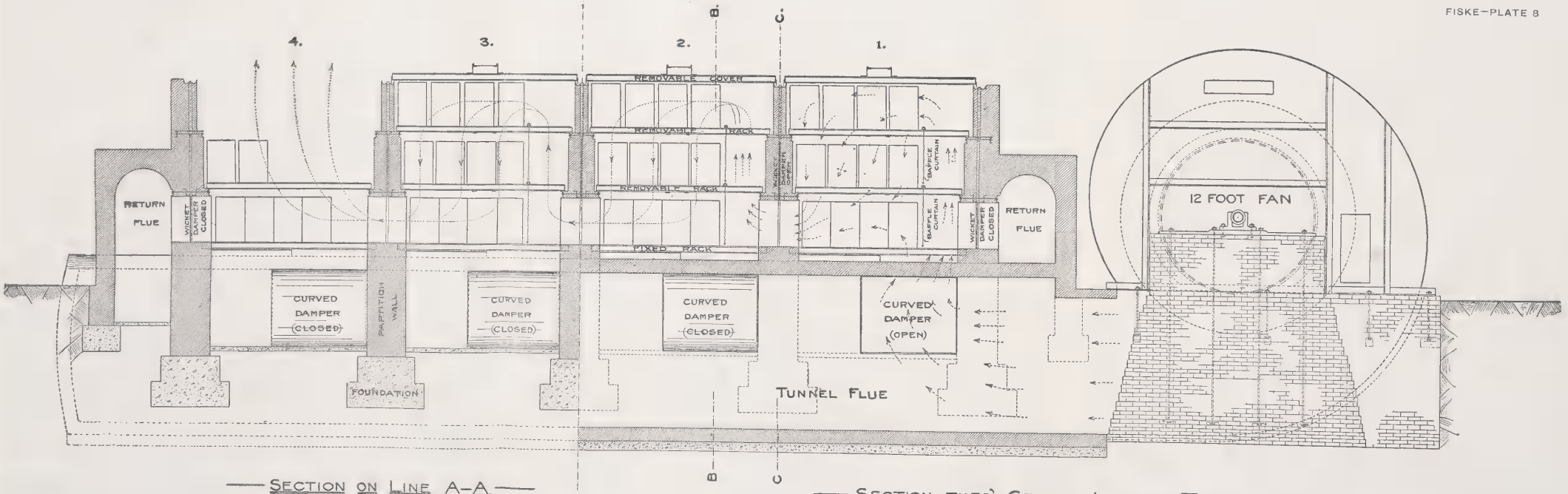
In the case of the Dover Point plant, some high grade

bricks are obtained by assorting, and consequently a second hand operation is here introduced, the burned bricks being deposited upon an assorting stand at the end of the kiln.

In the plant as thus far constructed no labor-saving appliances are used in connection with storing or loading the bricks, but it is the intention of the company to increase the main building to about twice its present length and to construct more continuous kilns similar to the one now in use. A storage building will then be constructed at right angles to the present main building, and an electric overhead crane arranged to take the bricks in large loads after assorting and to place them in the storage building, later to be shipped either by rail or water to the distant market. The elevated crane track in the storage building will be extended to include the railroad tracks at one end and the shipping dock at the other, and the assorted bricks will be handled on cradles, each containing a cart load. The cars or shipping barges may then be run under a crane at the point of destination and the cradles of bricks lifted as a unit and placed in the delivery wagons, thus eliminating the usual expense of hand labor for loading. By this system it is therefore possible to manufacture common bricks and deliver them to the customer with but two manual handlings from the clay bank to the mason, one after molding and one after burning, thus reducing the total labor to a fraction of its present amount even in the most modern yards.

The plant under discussion has so recently been put into operation that I am unfortunately unable to present any data as to the cost of manufacture, but it will doubtless be sufficient at this time to say that the practicability of the entire scheme has been fully demonstrated and that no great difficulties have been encountered. At a later date I hope to have the pleasure of presenting some data as to the cost of handling by this system and of burning in the continuous kiln with portable mechanical draft.

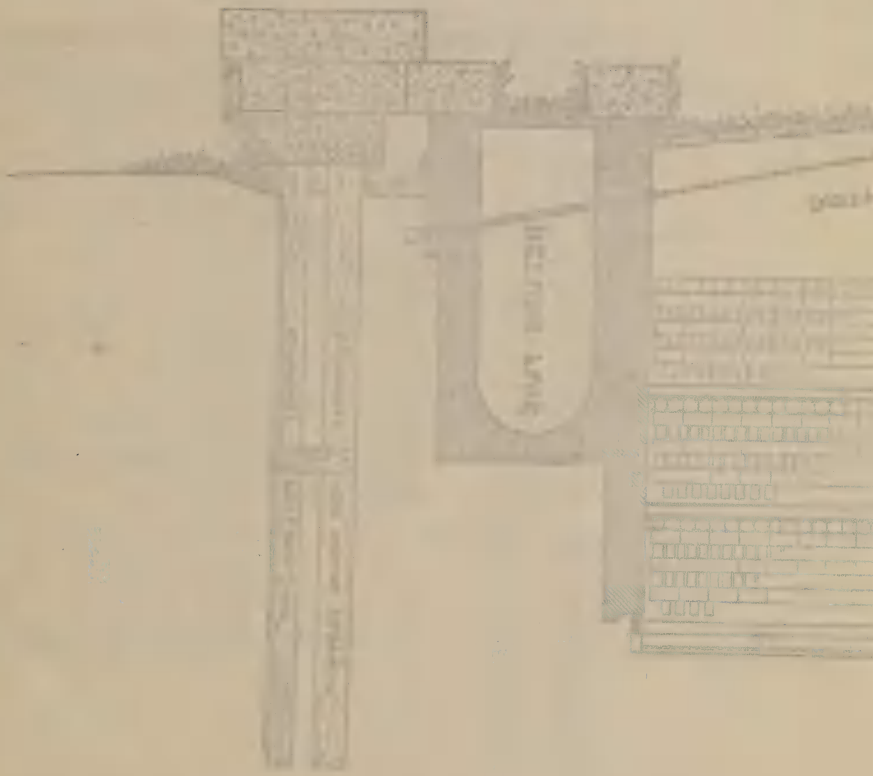
The preparations of the drawing and the erection of the plant has been under the immediate supervision of the Consulting Engineer of the Company, Mr. John C. Ostrup, member Am. Soc. C. E., well known throughout the country from

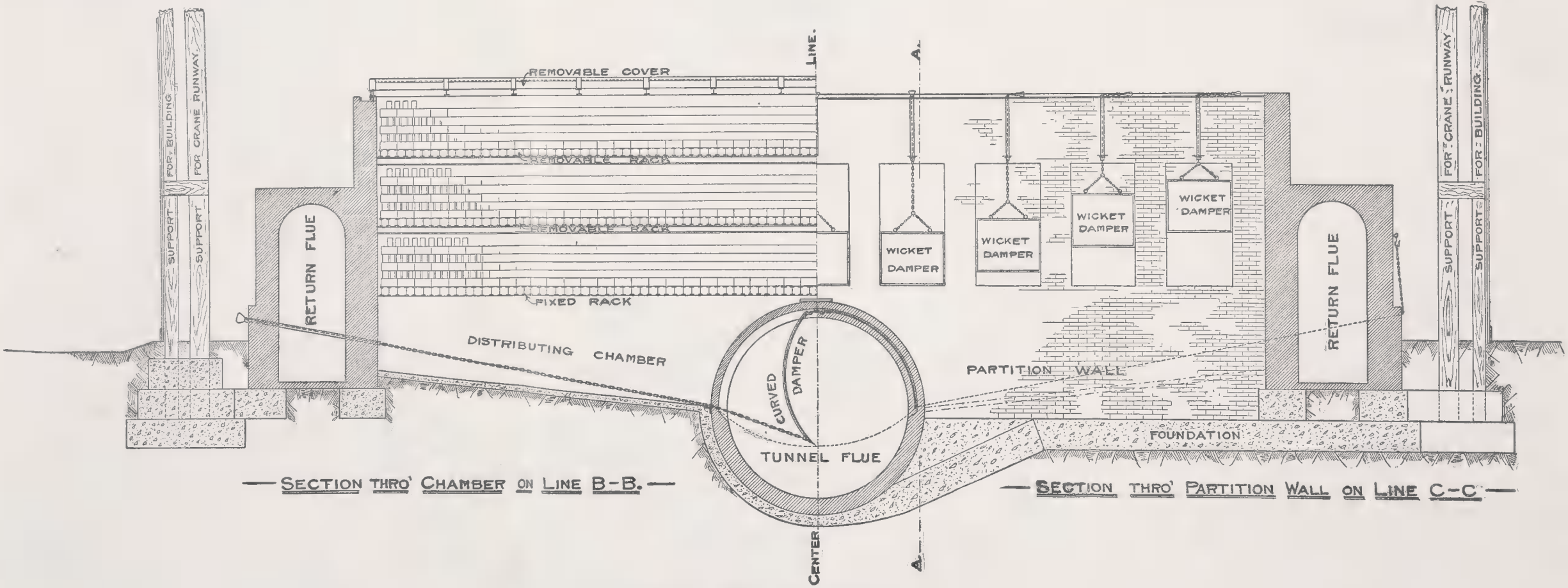


SECTION ON LINE A–A

SECTION THRO' CENTER LINE OF TUNNEL FLUE

SECTIONAL ELEVATION OF THE FISKE DRYER.

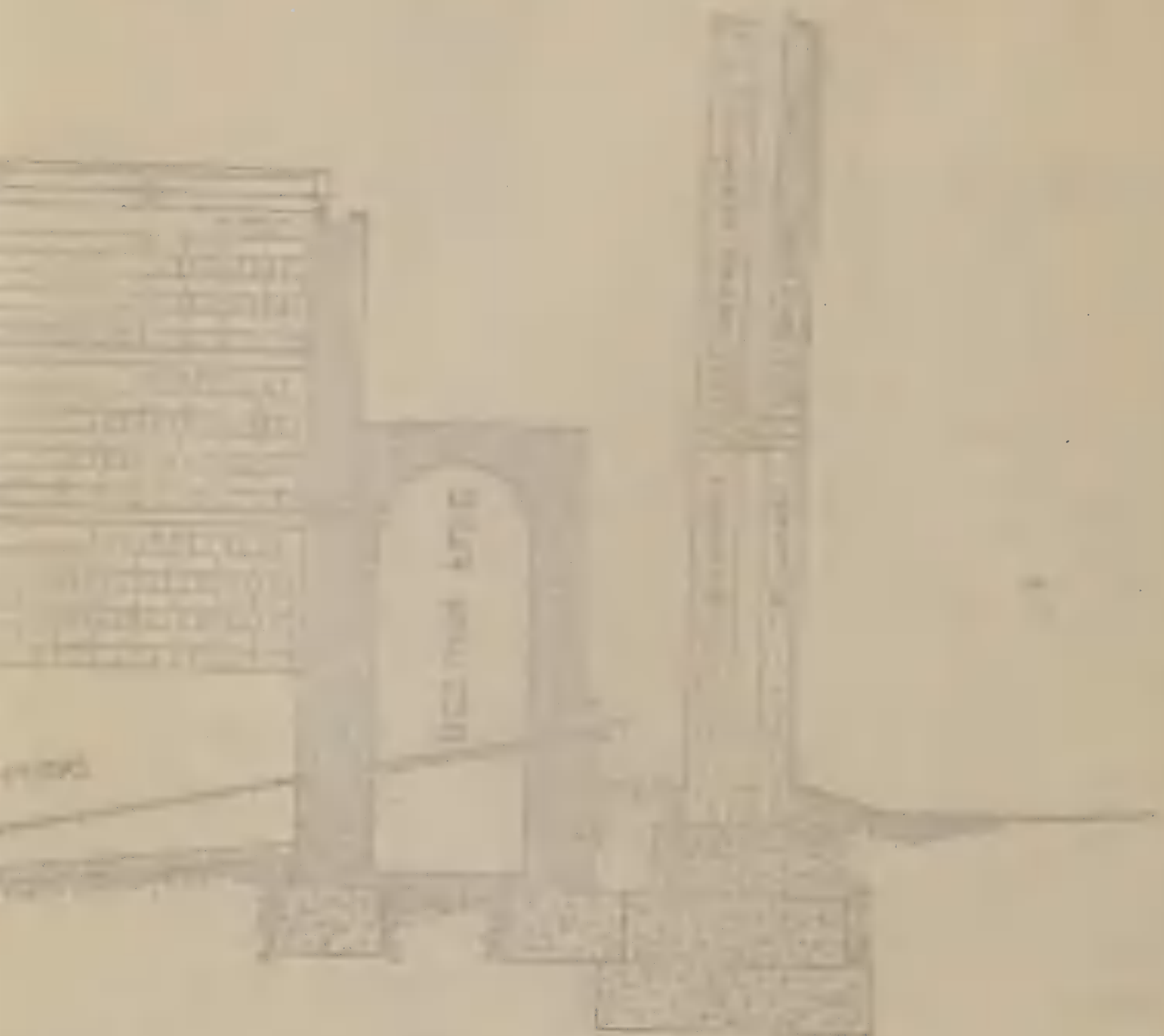




— SECTION THRO' CHAMBER ON LINE B-B. —

— SECTION THRO' PARTITION WALL ON LINE C-C —

CROSS SECTION ELEVATION OF FISKE DRYER.



his connection with the Chicago elevated roads and as Designing Engineer of the Boston elevated railroad.

DISCUSSION.

Professor Edward Orton, Jr.: Inasmuch as several months have elapsed since the publication of this paper,* and Mr. Fiske has been running his plant in the meantime and thus gaining new experience, I would ask him whether he has any statements which he wishes to add to those which have been already published on this paper? If so, it would be proper to make them now.

Mr. J. Parker B. Fiske: The secretary has been corresponding with me quite insistently for several weeks in regard to furnishing some figures in connection with the cost of making brick at our plant by the new method. I have told him that our plant has been put into operation so near to the time of this meeting that we are not able to present any figures which I really think would do justice to the plant, as it stands today. We have no records which represent the operation of the plant over any considerable period of regular manufacture.

I presume it is hardly necessary to say to those who visited the plant and saw what we are doing, that a plant as novel as this, and representing practically a new conception of brick making, could hardly be expected to be put into steady, systematic operation within two or three months after the construction was completed. As a matter of fact, we commenced regular brick-making operations about the first of November. We have been through the usual category of troubles incident to starting a new plant. I think I am right in saying that in starting a manufacturing plant of any kind, even of the most ordinary nature, that difficulties of some sort or other are almost inevitable for a time until the plant is brought down to a good working basis.

We are just emerging from the development or experimental period in our plant. For instance, we have burned

* NOTE BY SECRETARY: This paper was printed and distributed to the members of the society as advance sheets on December 10, 1902, and discussion at the Boston meeting specially invited. Also, the members visited the plant in a body on Tuesday afternoon, February 3, 1903, the day before this discussion was held.

our continuous kiln only four times. The first time was practically the drying out or burning out of the kiln. That suggested some changes which have been made, coincident with the further burning of the kiln, and they have been made, of course, at the expense of rapid and economical burning, because the masons naturally interfered more or less with the burning.

So far as the handling of the brick is concerned, we have proceeded far enough with that to feel pretty sure of what we can accomplish. I may say that the figures, in a general way, will be as follows: With the size of unit stack we are now handling, fifteen hundred brick, and with the speed of hoisting and travel to which our crane is now adjusted, we find we can handle fifteen hundred brick from one point to any other point in the factory, making the round trip in about five minutes. That requires the services of a crane man, part of the time of a helper, riding on the brick lift. On that basis we have repeatedly set a chamber of 18,000 brick in the continuous kiln, with two men, in one hour's time. That is at the rate of 180,000 brick handled into the kiln in ten hours by two men, or at the rate of 90,000 handled by one man in ten hours.

I think that a fair statement would be that a kiln setter, with three or four wheelers from an open yard, will handle 20,000 brick in about ten hours' time: four men, 20,000 brick in ten hours, or, one man, 5,000 brick in ten hours, as against one man handling 90,000 in ten hours by our method. That is a ratio of efficiency of 18 to 1.

Now, there is, of course, a large amount of other work which the crane has to do. It must handle the kiln covers, drier racks, drier covers, etc., all of which somewhat reduces its capacity for handling brick.

In regard to cost of operating the drier and kiln, my previous remarks will hold true, and we cannot give any figures which we think would represent what we will ultimately be able to do. I have no objection to telling people what we are doing, however, and I will say that we are operating our Crown Heat Generator with about 150 pounds of coal for each thousand brick dried. That, I feel certain,

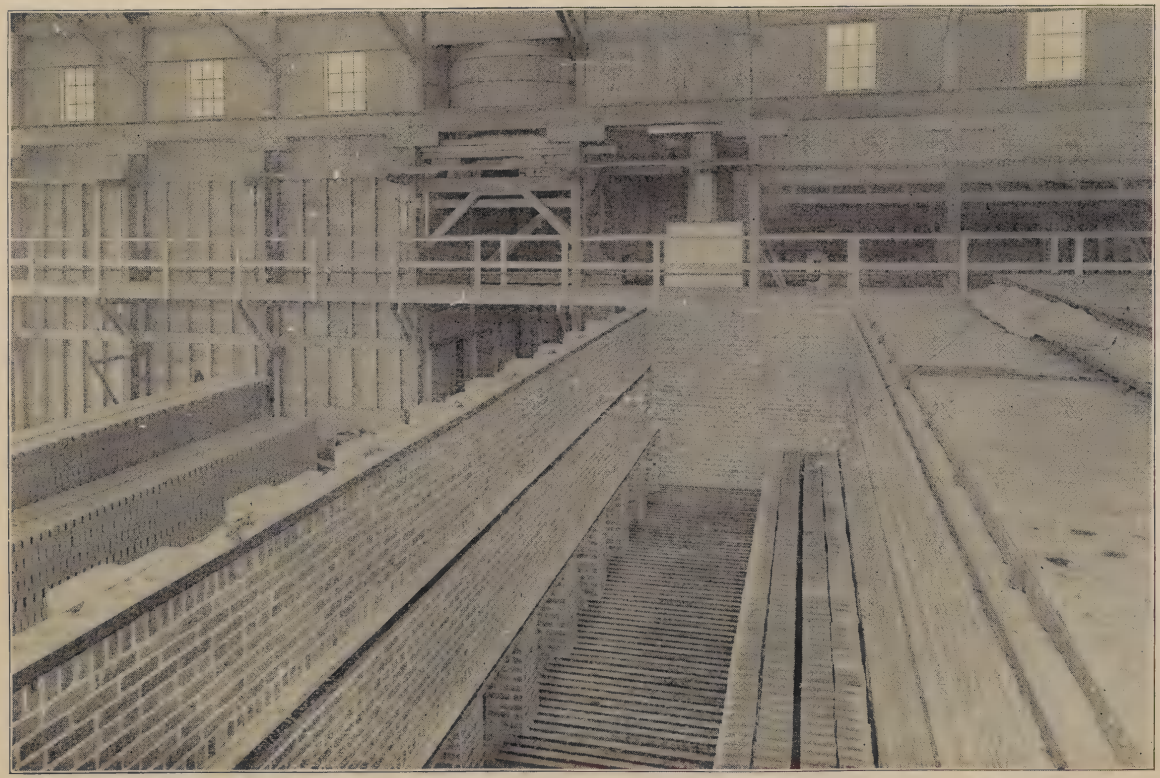


PLATE 10.—LOOKING DOWN INTO DRYER CHAMBER, THE COVER AND TWO PORTABLE RACKS BEING REMOVED. TWO STACKS OF SOFT BRICKS ARE SHOWN, PLACED IN POSITION FOR DRYING.

does not represent the ultimate economy. The designers and builders of the heat generator guaranteed, with one pound of water in each brick, to dry 1,000 brick with 100 pounds of coal, which, of course, is a small amount of fuel. The way in which the drier does its work is not very different from the ordinary progressive drier, where the source of heat is fixed and the ware is progressed through to the zone of maximum heat. In our case, it is impossible to progress the bricks, so the zone of maximum heat is progressed through the bricks. Thus, we get the same progression of temperature on the bricks in our drier which is found necessary in other driers. The hot, fresh air is not turned directly on the soft, green brick, but turned first on the brick which are nearly dry, progressing forward to the bricks which have been freshly put in the drier.

As I said, we have not yet operated the kiln under favorable conditions, but I have a report which was handed me yesterday on one of the chambers which has just been finished, on the fifth burn. The amount of coal burned in that chamber was 6,630 pounds, the chamber containing 18,000 brick. That is about three hundred and sixty-odd pounds of coal per thousand brick. I feel very sure that this will be reduced to at most three hundred pounds, but am not able to give further figures as yet.

I think that is all I have to say now, but I will be glad to answer any questions which any member may desire to ask.

Mr. Willard D. Richardson: The fact that this paper has been before us for several weeks and also the fact that my name has been upon this program as one of the persons expected to discuss it, would preclude any plea of insufficient time for preparation. Before leaving for this convention, I had the excuse that I had not seen the plant and so left preparation for discussion until after the trip to Dover Point; and while it was possible to have made preparation since visiting the plant yesterday, it has not been practicable.

I am glad, however, of this opportunity to express my appreciation of the work which has been done by Mr. Fiske at the plant at Dover and I feel the whole brick-making industry is indebted to Mr. Fiske for the large experiments he

has carried on there. Whether it will result in the repetition of such a plant in other places on substantially the same lines or not, the work he has done will lead to a great advance, I believe, in the economical manufacture of common brick. It will stimulate other efforts, perhaps along other lines, to accomplish what Mr. Fiske has been endeavoring to accomplish; that is, to eliminate hand labor in brick making.

After looking over the plant yesterday, I attempted to make some figures myself, but I found I could not make any figures which would be at all satisfactory as to the saving that might be accomplished by this system, and I can easily understand why Mr. Fiske cannot give any figures which would be of any value as to the saving actually being made at the present time. He knows, however, better than we can, how much his plant has cost above that of a modern plant of equal capacity having the car system, tunnel driers and continuous kilns; also whether the exhibition made to us yesterday represented the average daily operation of the plant, whether the chambers we saw open showed exceptionally good results or otherwise, whether the burned brick can always be picked up from the chambers as easily as we saw it done; whether the crane has already caused expense for repairs and whether the kiln covers are expensive to keep up, etc.

I have come up against this same problem of reducing hand-labor and studied a great deal merely upon the question of how to do away with the wheelbarrow—the hard labor of the wheelbarrow. Several times I have studied out and designed conveyors which would do away with wheelbarrows. My plans looked all right and I have been on the point of applying them to the carrying of clay and brick. But after making accurate calculations I always came back to the same conclusion, that upon the scale of operations which I have been conducting, while I could easily eliminate the hard work of the wheelbarrow, I could not save any money by it. I could not save a dollar by it, and so long as that labor is to be had, so long as men wanted to wheel the barrow every day, I continued to use the barrow.

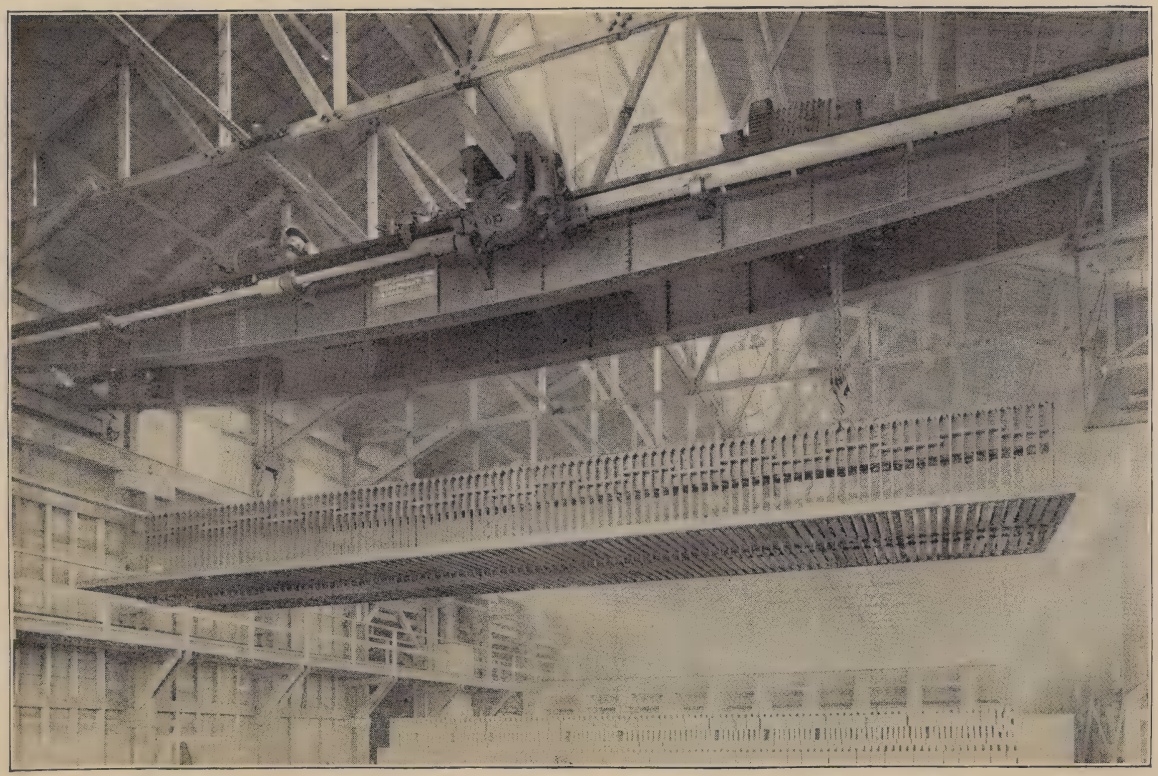


PLATE II.—CRANE HANDLING PORTABLE DRYER RACK.

So in Mr. Fiske's system, in order to show a saving of money by the saving of hand labor, the operations must be conducted on a large scale. When he has his plans completely carried out at Dover Point, he will probably be able to show a large saving and a profitable business, but I cannot figure such to be the case in the small experimental plant he has now in operation—small, not in most of its appointments nor in its fixed expenses, but in its daily output.

Mr. Ellis Lovejoy: There is a great deal of credit due Mr. Fiske for the work which he has put into the development of this process. I had some talks with him while he was working it up, and I must confess that through it all I thought he was on rather a wild goose chase. I want to say to him now, that seeing the plant in operation yesterday was quite a surprise to me. I did not expect to see the work carried on as smoothly and with as little difficulty as was done. I am frank to admit that he can handle his unit of fifteen hundred brick from the machine to the dry house, from the dry house to the kiln, and with the clay he is burning, from the kiln to the stockyard. There are some clays, however, which would give him trouble. If, however, the work is limited to common brick, made from clay which will not stick, the process can be carried through from beginning to end.

What improvements he can make to take in all other lines is a question for the future. But I am glad to know he has succeeded in working out the mechanical difficulties which to me, in the beginning, appeared serious. The question with me all along has been the possible power of the crane. We timed it a number of times yesterday and found it would make the trip in from three to five minntes, and I am willing to concede to Mr. Fiske that it could do the work continuously in that time. In Mr. Fiske's figures, he gives it as within its power to handle 180,000 bricks. He means, I think, green bricks from the machine to the dry house; the second handling to the kiln reduces the quantity to 90,000; and the third handling, from the kiln to the finished product, including dead work, reduces it to 45,000. I think this is the figure which Mr. Fiske gave me as the capacity of the

crane per day—45,000 finished brick. Notwithstanding the number of trips the machine would have to make, bringing in the coal, changing covers, moving racks and removing ashes, I am satisfied that it could handle this product of 45,000 bricks in one day. The whole value, now, of this process, hinges on that one point. If 45,000 is the limit of his crane, then there can be no increase in the system without introducing another crane.

Now, there is no saving up to the point where his bricks are put upon the racks. In that, I think, all will agree. He has two men with the crane to take the 45,000 brick to the kiln. Two men, with properly constructed trucks, will move the same quantity on cars through the dry house to the kiln. So, as I look at it, there is no saving whatever up to the point where the bricks reach the kiln. At that point in the old method, we must introduce setters and tossers, and just there I am free to admit I am a little lame. I am not familiar enough with common-brick business to know just what is required for a days' work in setting. I have heard of instances where a single setter put over fifty thousand bricks in a kiln in one day. I think it is common practice to put at least thirty thousand. But let us assume that he puts in twenty-two and a half thousand. Then it will take two setters to take care of the bricks that this crane would handle. It will take two or three tossers to deliver these bricks to the setter. If I am wrong in my estimates, I hope those who are familiar with the subject will correct me. The two setters and three tossers would cost about nine dollars a day, depending on the rate of wages, which would amount to twenty-seven or twenty-eight hundred dollars in the course of the year.

To offset this, Mr. Fiske has introduced an expensive piece of machinery, the crane itself. I have not at hand any figures giving the cost of his crane or the building to carry it, but there is a considerable expense in the building and the crane over the cost of an ordinary yard kiln shed. If this excess of cost amounts to ten thousand dollars, then he has an investment of that amount, and that investment in business is worth from eight hundred to one thousand dollars

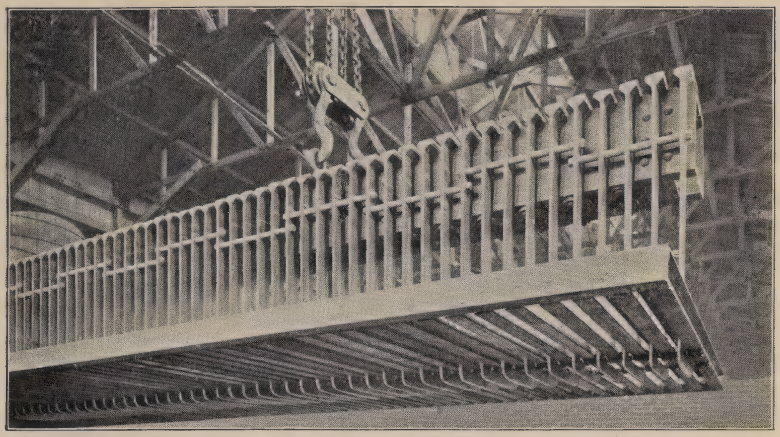


PLATE 12.—SHOWING HOW THE BRICK LIFT ENGAGES THE PORTABLE DRYER RACK.

PLATE 14 — BRICK LIFT DEPOSITING A STACK OF BRICKS ON KILN FLOOR BLOCKS; THIS WAS TAKEN DURING THE CONSTRUCTION OF KILN, BEFORE PARTITION WALLS WERE BUILT.

per year. If the excess is twenty thousand dollars, then he has money invested which represents an interest value in a factory of from sixteen hundred to two thousand dollars. If he has an excess of thirty thousand dollars invested, then he has interest cost exceeding the cost of labor to set the bricks. The difference in saving at that point hinges entirely upon the additional expense of his plant.

From that point on, his crane will move the brick to the sorting table. At the sorting table, as he is working at the present time, the bricks are rehandled, and in the plant as at present operated, there is no saving at that point, because the men who rehandle the brick at the end of the process could quite as easily take them from the kiln. We admit that he may have a saving up to the time the bricks are set in the kiln, of from sixteen hundred to two thousand dollars per year. As the plant is at present operated, there is no saving beyond that point, but if he introduces his system at the finished end of his product, and, by the use of cranes instead of wheelbarrows, can handle his product and save the wheelers, there is a possibility,—a great possibility,—of more than doubling the saving he would make in setting the green bricks. In view of the unfinished state of his plant, we must give Mr. Fiske the benefit of this possibility.

As the plant is at present constructed, it has a machine capacity of sixty thousand, a crane capacity of forty-five thousand, and a kiln capacity of eighteen thousand brick per day. It may be possible for him, after a little experience with the kiln, to increase the rate at which he is now burning, and turn out the equivalent of a chamber and a half per day, which would bring it up to a little over one-half the capacity of his crane. I think he can do this. Now, then, to get his unit of 45,000 bricks,—the full capacity of his crane,—he must radically change the structure of his kiln. I do not believe Mr. Fiske is satisfied with the kiln part of his plant, and, no doubt, he already has ideas, based on his experience with this kiln, which would greatly improve that part of his factory. He cannot lengthen it without lowering the capacity of his crane. The thought was suggested by Mr. Richardson that he can put another kiln on the other

side of his machine, and this would not increase the distance his crane would have to travel; but that brings into the question the handling of the burned product at two points, and would mean the introduction of two cranes, so it seems to me that it is not to be considered.

I am not prepared to give any expression of opinion regarding the life of his kiln as compared with that of other continuous kilns, nor am I prepared to give any comparison of cost between his kiln and other continuous kilns; but those items of cost, if greater than that of other continuous kilns, increases the amount of money invested in the business and lowers the difference between the cost by this process and the older method.

He undoubtedly makes a great saving in fuel over any other system using common kilns, either up or down draft; but I do not think Mr. Fiske will claim any unusual saving in the use of his kiln over other types of the continuous kiln.

So the whole matter hinges upon the value of the crane in replacing the labor of the old method.

Mr. Fiske: In answer to some points made by Mr. Lovejoy, I will say that the plant, as it stands today, is of course not finished; and for that reason we do not claim to be making anything like the saving over the usual methods which we expect to make when the original conception of the plant is carried out. In plants making common brick only, which are the kind of plants where I think the greatest saving would be made, there is no sorting of bricks to be made at the finishing end of the plant. In that case, the bricks would be brought directly from the kiln by means of the crane, and either loaded directly on the cars by the crane, or put upon a loading belt which has cleats or bars across it, as in case of the drier racks, moving forward like the ordinary conveyor belt and loading into cars outside of the building.

I want also to say that the crane as we now have it in operation is not doing anywhere near its maximum work. I understand it is the practice in the large steel mills to have a speed of travel on the track of six hundred feet in a minute. Our speed is somewhat less than two hundred feet

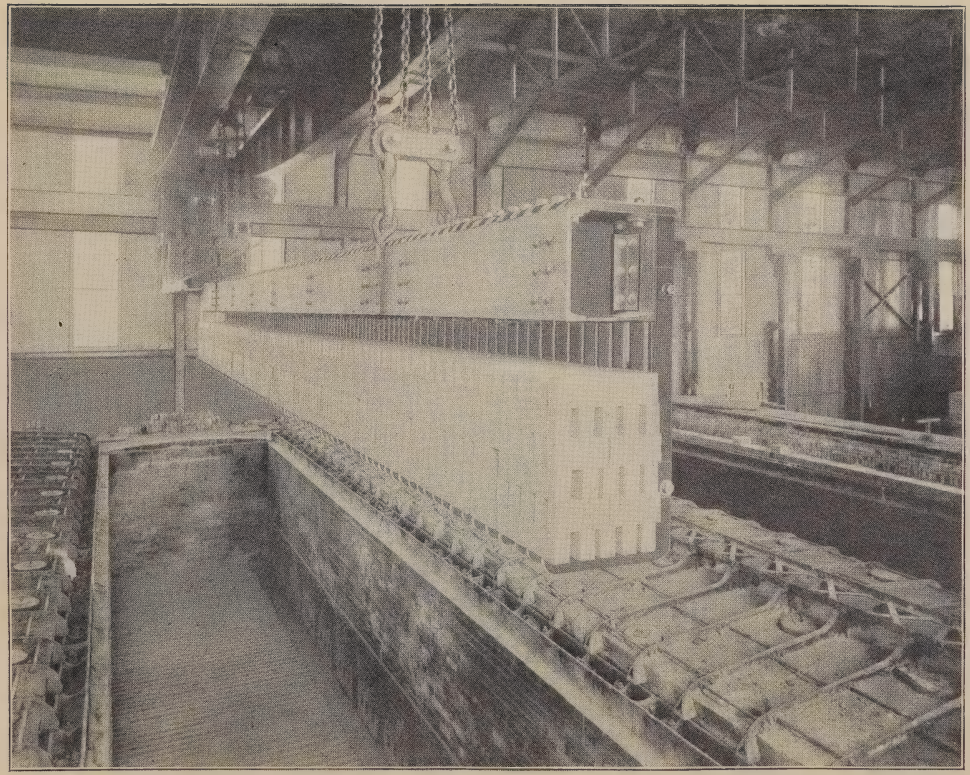


PLATE 13.—KILN CHAMBER WITH CROWN REMOVED, AND THE CRANE WITH STACK OF DRIED BRICKS READY FOR DEPOSIT IN THE KILN.

a minute at the present time. We have it so arranged that the crane may be speeded up later when necessity requires. The speed in hoisting can be in the neighborhood of twenty feet a minute for a load similar to the one which we carry. Our speed is some five or six feet a minute. So the value of the crane in this industry cannot be judged by the amount of material which we are actually handling today at Dover Point. It is a well known fact that the electric traveling crane, as much as any other one thing, has revolutionized the steel business, and the electric traveling crane has been found to be, of all the different devices so far invented, the most efficient for handling large masses of heavy material.

I do not wish to repeat things which I have said in my paper already presented to the society, but I do want to say this: that looking over the different manufacturing fields, it has been my belief for a long time that no field required the introduction of machinery for handling its product cheaply more than the brick business; because bricks, of all finished products in the world, are worth the least per ton of anything I know.

In regard to the cost of the crane and additional investment, I will say that our crane cost $4,200. That does not include the tracks, which I think cost some three or four hundred dollars. Five thousand dollars, as an outside figure, will represent the installation of the crane. It must be borne in mind, however, (or, I will have to ask you for the moment to take it for granted) that this crane will handle, say fifteen million brick per year. For handling any such product as that by the car system and tunnel driers, a large investment in tracks, turn-tables, cars, etc., must be made. That would go a long ways to offset the cost of this crane.

Moreover, the item of repairs and depreciation on the traveling crane is a very small factor; while we know that the cost of repairs and depreciation on the car system is a large factor and a very troublesome one. There is hardly a large plant today but has more or less of its cars in the repair shop. The extra cost of the building should not be charged to the crane, or to this system, because while it is true that we have a more expensive building than is put up on the

ordinary brick yard, we have a building which is more permanent, which will represent less cost for repairs and less depreciation, and is in the nature of an improvement itself independent of its connection with the crane. It is in the line of better construction, which I believe we are all coming to in the ceramic industries.

In regard to the capacity of the crane, as operated today, Mr. Lovejoy's figures are about correct. That is to say, we figure that the crane will do, on straight handling work, about 180,000 brick in ten hours for one movement of the bricks. As we have three movements, the number of brick will be reduced to one-third, or sixty thousand; and making liberal allowance for the time in taking the brick out of the kiln, handling covers, ashes, coal, etc., I think forty-five thousand is a fair estimate. In plants representing large investments, however, it is the custom to operate them more than ten hours a day; and the larger your investment, the more profitable it is to operate your plant overtime. It is our intention, when occasion requires it, to have this crane do a portion of its work at night. We have electric lights, and can see to do our work as well by night as by day; so the capacity of the single crane can easily be increased to sixty thousand brick in twenty-four hours.

The cost of the kiln has been touched upon, and I will say that no extra expense, over and above the ordinary kiln, is necessary by reason of this system. In fact, while some items are somewhat more expensive, as the kiln cover, the construction of the balance of the kiln is somewhat cheaper owing to the absence of doorways, complicated flue system, damper system, etc. There are many general advantages which we see in this system over the ordinary continuous kiln set by hand, and which operators of continuous kilns have appreciated. One is the ability to uncover the burned bricks when the burn is completed, by taking off the entire cover from the kiln and thus allow it to cool quickly, and allowing plenty of light and air for the men necessary to work in the kiln. One great disadvantage of the continuous kiln today is the fact that the men have to work in the hot, dark kiln chamber, isolated from the rest of the operators,

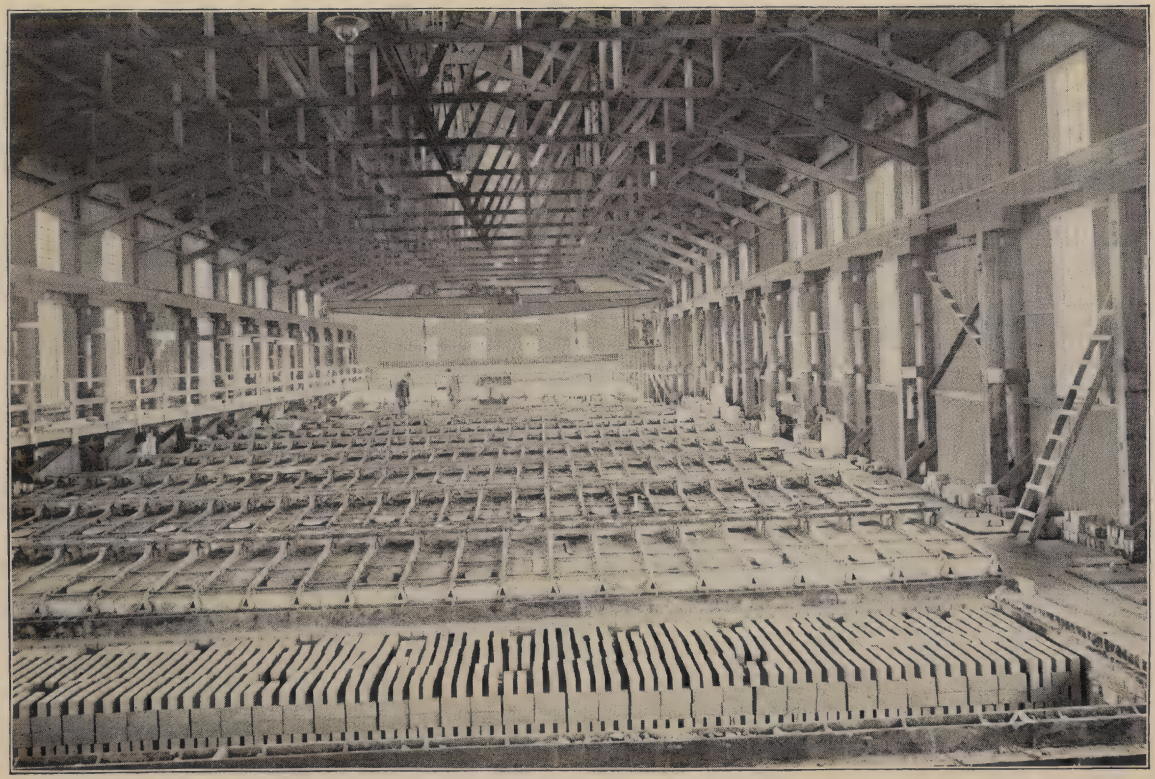


PLATE 15.—KILN WITH CHAMBER OF GREEN BRICK IN THE FOREGROUND READY FOR RECEPTION OF KILN COVER.

and not directly under the eye of the superintendent; and their work probably costs more than it would in other parts of the plant. In case of the kiln with removable covers, there is a better place to work and the men are immediately under the eye of the superintendent.

With the increase of speed which is perfectly practical in connection with the crane, there will be no difficulty, so far as we have been able to judge by our experience so far, in providing extra kiln capacity by lengthening the kiln in the present direction, which is in accordance with our original plans. It would not be practical to build another kiln at the other end, because of the difficulties which Mr. Lovejoy mentioned.

Prof. H. A. Wheeler: I think Mr. Fiske is entitled to the highest compliment for the bold, courageous, and very successful way in which he has started on this new trail; and I think it was unfortunate that we were so kindly invited to go out to inspect the plant when there had been such a limited time in which to get it into smooth, working condition, which requires such a long time in any industry. We are all aware of the fact that before any concern becomes money-making, besides the first investment of capital, and the investment of capital to carry on the business, the working capital, there is another investment necessary which sometimes exceeds the other two, and that is for effective organization. It is something which even engineers often overlook entirely, or at least largely neglect to take into account, and which very few capitalists ever realize the importance of. The building up of an effective organization is something which is seldom done under one year, and often it requires several years. So I want to express my hearty appreciation, not only of Mr. Fiske's courage, but of the smooth, successful way he has got the plant in operation in the very limited time since the construction was completed. While I very much enjoyed Mr. Lovejoy's criticisms, I must say that Mr. Fiske is blazing a trail which is going to prove of much greater importance in the future than now appears. Then there is increased insurance rate, extra cost of wear and tear, and similar items which Mr. Lovejoy has overlooked as pertaining to the old

method, which will materially increase the comparative saving.

Its elimination of a large number of laborers will in the future make it valuable. The labor problem is becoming a very serious one in this country, and anything which tends to eliminate the slavery of the walking delegate which is going to enable us to carry on our business as we may wish, free from the control of the labor master, is going to mean the differences of success and failure. That thing alone, in the future, is likely to become much more important than any mere slight saving above the cost by another method. The recent anthracite strike is a mere rumbling of the battle ahead. We can always control a few men. In any well managed organization, if the foreman has any tact and diplomacy, there are always a few reliable men who may be depended upon. But when it comes to the control of masses of these laboring men, we are up against a serious question. As the labor organizations become more and more powerful, with leaders in some instances of very high ability and generalship, the question becomes more serious, and anything largely reducing labor perils, enabling us to get along with fewer and fewer men, is going to be the only successful way for handling the labor problem in the future. The great engineering strike in England is what really put this nation where it is today in its industrial condition and gave Germany the enormous advantage which it now holds, putting England back to third place where it was unquestionably first. It was the walking delegate who caused England to drop behind to third place, and it is the walking delegate today who is rapidly making America's industrial condition more and more unsafe, and making capital more and more conservative as to engaging in manufacturing enterprises.

Professor Orton: I am not going to attempt to discuss the merits of Mr. Fiske's plant, but there are statements of Mr. Richardson and Professor Wheeler which I can not allow to pass undisputed. I do not believe that any permanent good is going to come to the human race by an attempt to accomplish by mechanical effort what is now done

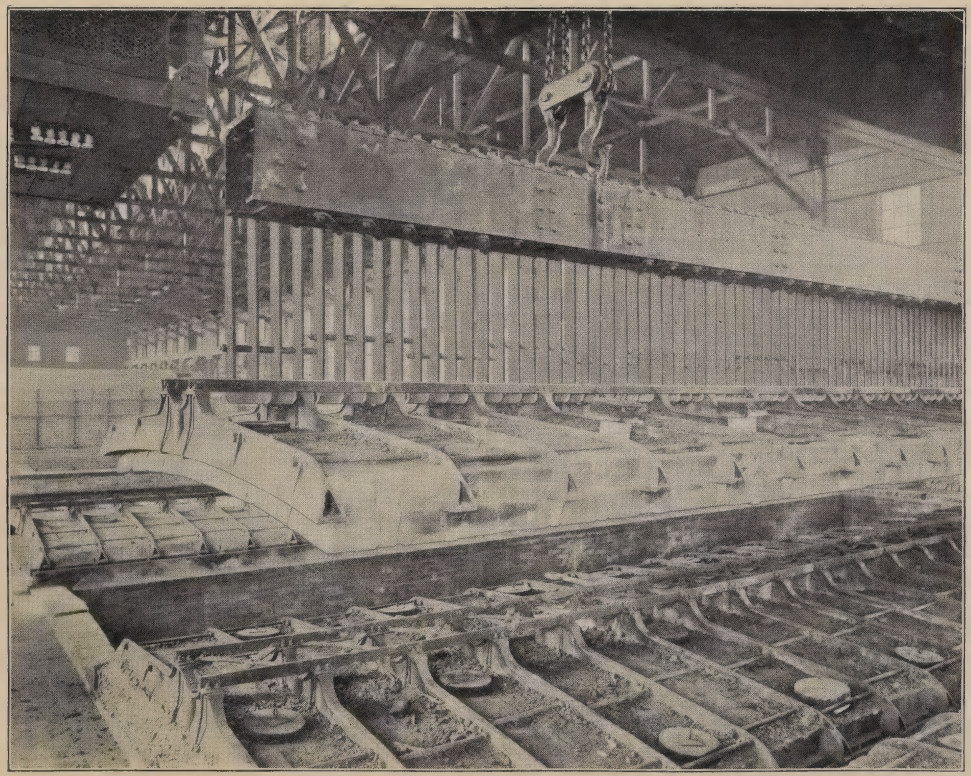


PLATE 16.—REMOVABLE KILN CROWN BEING HANDLED BY CRANE AND LIFT.

by hand labor. Mankind is here and must have a living. Men must have a certain amount of physical exercise, a certain amount of work. Any way which provides mechanical means of making money, without depriving man of the opportunity for work, is to be commended; but to actually supplant labor by machinery seems to me a superficial way of treating the labor problem. You cannot perform work mechanically except by the combustion of fuel. Of course, there is a moderate supply of water power which we may use more in the future, and we may use wind power more than now. But as things are now constituted, the bulk of our power comes from combustion of fuel. The heritage of fuel which we have is something which is not growing and increasing. The fuel which we are now using is largely stored or fossil fuel. Mr. Richardson has stated that wherever it is possible to do a thing mechanically at the same cost that it can be done by labor, it should be done by the mechanical method. I would take exactly the reverse stand. I would do by hand labor, everything which can be done best that way, and only do by machinery that which the good of the human race requires to be done in that way. If in one case a great economy results from mechanical methods, so that an industrial product can be turned out at a less cost, and thus reach more people, and provide more comfort to more people, then let the mechanical means be employed. But if the cost of the two methods is just the same, then I say give labor the work. Instead of attempting to get rid of the slavery of the walking delegate by substituting mechanical means for hand labor, rather try to get closer to our brothers of the laboring class, and develop in them and in ourselves humanitarian principles and sane coöperation, by which alone a permanent improvement can be made.

Mr. W. D. Richardson: I desire to correct a wrong impression which may have been made by what I said awhile ago regarding hand labor. If a man can make improvements in brick manufacture which will eliminate hand labor, even if not effecting a great saving, I believe it ought to be done. It is something which ought to be done in

manufacturing lines all the way through. If this improvement lessens labor and can be operated without greater expense to the company than the employment of hand labor, including of course, interest, repairs and depreciation, it ought to be adopted.

I base this statement upon humanitarian as well as economical grounds, not with any idea that the elimination of hand labor is going to solve the labor question, only insomuch as the accomplishment of laborious operations by mechanical means tends to elevate any industry and to place all who labor upon a greater equality. We cannot eliminate the laborer, and the labor question must continue to demand wise and careful consideration. But to increase the production per man, in any line of work, and at the same decrease the hard manual labor involved, cannot but be moving in the right direction and lead to a shortening of the hours of labor with greater comforts to all. Let no one fear labor-saving inventions. The more that can be accomplished in any line with a given amount of labor the greater opportunity, for development in other lines and the better for the future welfare of the people of the whole world.

That is why I am especially interested in this attempt of Mr. Fiske's to save the hard hand labor in brick manufacture. Mr. Lovejoy has gone into the question very thoroughly—I knew he would—and we have a very fair estimate of what may be expected from the new system which Mr. Fiske has developed. Of course, in the figures which Mr. Fiske has given us in regard to the drier, kiln, etc., there is nothing especially pertaining to the Fiske system. The cost of drying brick has not been greater by the car system, nor is the cost of burning greater in other continuous kilns. One point I thought of yesterday which I want also to bring out, and that is the fact that the success of his system is not entirely dependent use of his continuous kiln. Any open top continuous kiln of sufficient width could be used, or, the labor of handling the brick could be saved by setting in the same manner in an updraft kiln. Of course, such up-draft kiln must have permanent arches under a permanent perforated floor. He could set a large kiln of brick of several

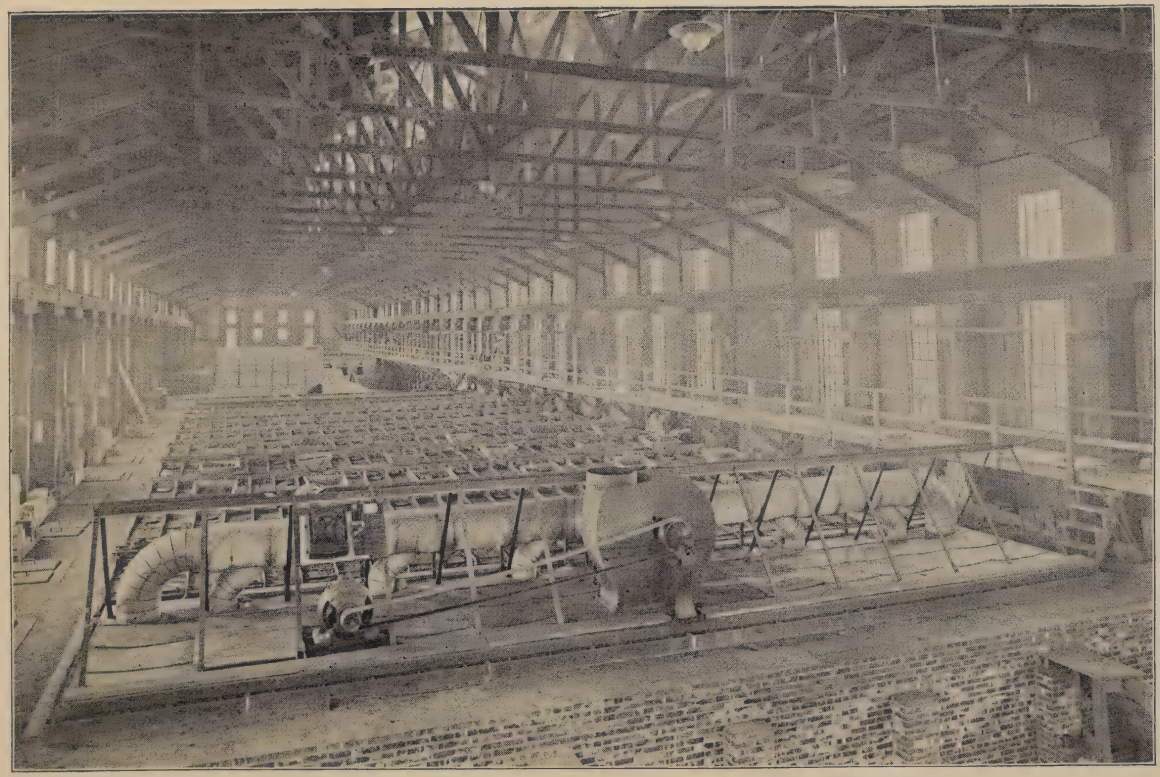


PLATE 19.—SHOWING PORTABLE DRAFT APPARATUS, IN POSITION ON THE LAST CHAMBER OF THE KILN.

hundred thousand and still have a saving in the labor of setting the brick.

At this point, however, we come to a stop in our calculations, for the difficulties of this system now begin, and we are in doubt about their being entirely overcome. There is nothing impracticable in handling 1500 or more brick with a crane, picking them up and setting them down wherever desired along the line of its travel. So that there is need of no further demonstration after what we saw yesterday to prove that brick can be set by this method cheaper than by hand. The greater problem, which I am unable to say yet has been successfully solved, is to construct a continuous kiln that will permit of being set in this manner and give good burns; or to construct any kiln in which brick from ordinary clays can be burned to a good degree of hardness and the brick so evenly spaced in their original position that they can be picked up again without serious difficulty by the fingers of the crane. When it has been proven that this can be done the system will be a success and will be sought after by others, and become an important factor in the brick business. I shall watch the solution of this problem with a with a great deal of interest. It is up to Mr. Fiske, and I wish him all success.

THE DEVELOPMENT OF THE "MATT" GLAZE.

BY

CHARLES F. BINNS, M. SC.

Some forty years ago, Mr. R. W. Binns, my late honored father, then the Director of the Royal Worcester Porcelain Works, conceived the idea of covering the brilliant surface of a porcelain glaze with a semi-lustrous or texture color. The intent was to check the strong reflections of a shining glaze and to impart a soft sheen which would combine harmoniously with furniture and drapery. The specimens executed were shown to certain buyers who refused to acknowledge in them any merit whatever. Nothing daunted, the originator set the work aside, saying that some day it would be sought after.

The prophecy was fulfilled about fifteen years later. Dead surface ware was demanded and produced with an unparalleled success which lives in the memory of many, and which resulted in the term "Royal Worcester" being regarded as synonymous with dead or matt colors.

The idea of dull surface was taken up by artists, to whom it specially appealed. Architects specified dead glaze for interior tile work as well as terra cotta, and manufacturers all over the world sought to supply the need.

A variety of expedients were resorted to in order to produce the required dullness. The attack of fluoric vapors, abrasion by sand-blast, an immature glaze, have all been tried, and it is not to be wondered at that manufacturers who have had no other resource have abandoned the pursuit in despair.

When I began to investigate the problem, the thought of devitrification was present. It is well known that a highly acid glaze, low in alumina, will, if cooled slowly, lose its gloss, presenting a surface more or less dead and sometimes

even iridescent. But experiments embodying this idea did not succeed, probably because an attempt was made to burn the glazes in a general kiln and the cooling was not slow enough.

The matter stood at this point when the date of our last annual meeting came around. On that occasion Francis W. Walker presented his paper on copper greens. Among his numerous examples there was one which started a train of thought the end of which is not yet.

This glaze differed in appearance from others in the same series, by reason of the fact that it possessed a delicate texture surface. Not merely dull but soft and silky. The touch brought back vividly the memory of the Worcester ivory, and perhaps this helped to deepen the impression. Turning to the formula of the glaze in question it was found that the essential difference from its fellows lay in the content of Al_2O_3. This stood at .35 and the figure opened a new world.

In passing, one may point out that this fact is a remarkable illustration of the value of thinking in formulæ. By no other possible means could it be known that the figure was at all unusual at the heat used or would it have conveyed any idea.

That night the matter was turned over and pondered, even to the "wee sma' 'oors" — "Alumina 0.35" repeated itself over and over until the resolve was taken that the point should be threshed out.

Several questions presented themselves—

1. Does the alumina content govern the production of texture?

2. Will the same alumina content produce the same result with different bases?

3. How far will the acid content affect the result?

4. To what physical or chemical cause is the texture due?

As a means of answering these questions the following base combinations were arranged:

1	PbO	0.7	2	PbO	0.7
	CaO	0.3		CaO	0.2
				ZnO	0.1
3	PbO	0.6	4	PbO	0.55
	CaO	0.2		CaO	0.30
	ZnO	0.2		K_2O	0.15
5	PbO	0.5	6	PbO	0.5
	CaO	0.3		CaO	0.2
	ZnO	0.2		ZnO	0.2
				K_2O	0.1
7	PbO	0.5	8	PbO	0.5
	BaO	0.2		CaO	0.2
	ZnO	0.2		BaO	0.2
	K_2O	0.1		K_2O	0.1
9	PbO	0.5	10	PbO	0.5
	CaO	0.2		CaO	0.1
	BaO	0.2		BaO	0.1
	ZnO	0.1		ZnO	0.2
				K_2O	0.1

Each of these bases was made up in two extremes, one having alumina 0.25 and the other alumina 0.50, the content of silica being maintained at 1.60, the amount in the Walker glaze.

All the mixtures were made as raw glazes and ground in a ball-mill. It will at once be seen that the idea here was to find the content of alumina which produced the best texture with each base. The specimens shown consist of the two extremes and the best intermediate in each series. The composition of each mix is given. The extremes were weighed up and ground. They were then dried and the proportionate equivalents weighed out. Mucilage was freely used in order to secure a thick body of glaze, and the trial pieces consisted of tile furnished by the Beaver Falls Art Tile Co. All except the first series were fired flat, the heat throughout being cone 01.

It is due partly to the nature of the body and partly to the horizontal position that so many of the glazes have tucked and parted. Similar glazes upon upright surfaces

and plastic bodies have been entirely free from this trouble, but it may be mentioned here that the difficulty almost always occurs in drying. If a matt glaze be cracked, or at all imperfect on entering the kiln, it will be unable to correct the fault. But if it be sound when dry, it will in all probability remain sound when burned.

The following table indicates the appearance of each glaze and the content of alumina at which the best surface was found, not always good, of course, but the best of its series:

No.	Lower Extreme Al_2O_3 0.25	Best Intermediate	Higher Extreme Al_2O_3 0.50
1	Semi bright	Slight scum, harsh Al_2O_3 0.375	Parted
2	Nearly bright	Dull matt, parted Al_2O_3 0.375	Parted, dead
3	Bright, scummed	Good matt, parted Al_2O_3 0.375	Quite dead
4	Bright, immature	Good matt, but scummed Al_2O_3 0.35	Quite dead
5	Bright, immature	Dead matt Al_2O_3 0.375	Quite dead
6	Bright but sluggish	Good matt, slight scum Al_2O_3 0.375	Matt but parted
7	Dead	Dead matt, good face Al_2O_3 0.375	Parted, infusible
8	Fine matt	Dead matt Al_2O_3 0.275	Dead
9	Good matt	Fine matt Al_2O_3 0.325	Dead, parted
10	Scummed matt	Good matt Al_2O_3 0.35	Quite dead

Reviewing the above it will be seen that the more complicated bases give the best results, and that the alumina content for a good matt is always close to the figure 0.35, varying slightly with the fusibility of the base. The glazes being raw, barium must be considered as less fusible than calcium. Barium seems to contribute towards a fine silky

texture, but will not carry quite so much alumina as calcium.

Assuming from these results that Al_2O_3 0.35 was about the most favorable content, certain other points were pursued:

No. 11 Interchange of bases. Two glazes 11-1 and 11-4 were made up and blended. The RO's were

$$11\text{-}1 \left\{ \begin{matrix} PbO & 0.575 \\ CaO & 0.425 \end{matrix} \right. \quad \text{and} \quad 11\text{-}4 \left\{ \begin{matrix} PbO & 0.575 \\ K_2O & 0.225 \\ ZnO & 0.200 \end{matrix} \right.$$

while the alumina and silica were 0.35 and 1.60 respectively in both glazes.

Three examples from the series are shown:

No. 11-4 is a dead matt with a beautiful crystal developed in the surface, working the glaze into a "crocodile skin" texture.

No. 11-2 has the formula

$$\left. \begin{matrix} PbO & 0.575 \\ CaO & 0.170 \\ K_2O & 0.135 \\ ZnO & 0.120 \end{matrix} \right\} Al_2O_3\ 0.35\ \ SiO_2\ 1.60$$

and is a fine matt glaze.

No. 11-3 is also a good matt, but badly parted, due to drying cracks. The formula is:

$$\left. \begin{matrix} PbO & 0.5750 \\ CaO & 0.2125 \\ K_2O & 0.1125 \\ ZnO & 0.1000 \end{matrix} \right\} Al_2O_3\ 0.35\ \ SiO_2\ 1.60$$

Of series 12, compounded on similar lines, three specimens are given:

No. 12-1, an interesting crystal glaze, bright rather than matt, contains

$$\left. \begin{matrix} PbO & 0.575 \\ CaO & 0.200 \\ ZnO & 0.225 \end{matrix} \right\} Al_2O_3\ 0.35\ \ SiO_2\ 1.60$$

No. 12-2, a beautiful texture matt, has

$$\left. \begin{matrix} PbO & 0.575 \\ CaO & 0.200 \\ ZnO & 0.135 \\ K_2O & 0.090 \end{matrix} \right\} Al_2O_3\ 0.35\ \ SiO_2\ 1.60$$

and No. 12-3, a very fine matt, has

$$\left. \begin{matrix} PbO & 0.575 \\ CaO & 0.200 \\ K_2O & 0.225 \end{matrix} \right\} Al_2O_3\ 0.35\ \ SiO_2\ 1.60$$

The next point to present itself was the influence of silica upon a glaze which possessed the constitution of a matt.

To throw light upon this the following series was laid down:

$$\text{No. 13}\quad \left.\begin{matrix}\text{PbO } 0.5\\ \text{CaO } 0.2\\ \text{ZnO } 0.1\\ \text{K}_2\text{O } 0.1\end{matrix}\right\} \text{Al}_2\text{O}_3\ 0.4 \left\{\begin{matrix}\text{SiO}_2\ 2.5 \text{ (higher extreme)}\\ \text{to}\\ \text{SiO}_2\ 1.2 \text{ (lower extreme)}\end{matrix}\right.$$

The latter of these gave a good matt as was expected, the former showed a distinct brightening of the surface and increased mobility, the significance of which will be pointed out later.

The best intermediate contained SiO_2 1.95.

The behavior of barium in the earlier trials had suggested that with this base a lower content of alumina would be advisable. A new series was therefore made up.

$$\text{No. 14}\quad \left.\begin{matrix}\text{PbO } 0.3\\ \text{CaO } 0.2\\ \text{BaO } 0.3\\ \text{ZnO } 0.2\end{matrix}\right\} \begin{matrix}\text{Al}_2\text{O}_3\ 0.40 \text{ (higher extreme)}\\ \text{to}\\ \text{Al}_2\text{O}_3\ 0.15 \text{ (lower extreme)}\end{matrix} \quad \{\text{SiO}_2\ 1.6$$

These are shown, together with an intermediate carrying Al_2O_3 0.225. The last named is somewhat hard; the lower extreme is a good matt, but the higher is perfectly dry.

Yet another series had for its objective the interchange of barium and calcium:

No. 15-1 contains

$$\left.\begin{matrix}\text{PbO } 0.4\\ \text{CaO } 0.3\\ \text{ZnO } 0.2\\ \text{K}_2\text{O } 0.1\end{matrix}\right\} \text{Al}_2\text{O}_3\ 0.35\ \ \text{SiO}_2\ 1.60$$

No. 15-2 has

$$\left.\begin{matrix}\text{PbO } 0.4\\ \text{BaO } 0.3\\ \text{ZnO } 0.2\\ \text{K}_2\text{O } 0.1\end{matrix}\right\} \text{Al}_2\text{O}_3\ 0.35\ \ \text{SiO}_2\ 1.60$$

The difference is very marked. No. 15-1 is a good matt though parted from drying cracks, 15-2 is hopelessly harsh and dry, while the best intermediate, carrying CaO 0.18 and BaO 0.12 is scarcely fused to a texture.

Reverting now to the questions propounded at the beginning of this paper, the enquiry may be made as to whether satisfactory answers have been found.

The scope of the enquiry has been somewhat limited, in that the influence of alumina has been pursued almost to the exclusion of other points, perhaps equally important. That alumina has a very large part to play in the production of matt glazes is undoubted. So far as this enquiry has gone, it may be said to have the most important part of any glaze constituent. In fact, that a good texture matt can always be produced by excess of alumina. What "excess" means depends upon the base used on the one hand and upon the acid content on the other. Different base combinations require different contents of alumina, but within comparatively narrow limits. Lead seems indispensable but an excess is injurious. Zinc is very desirable as are also potash and lime. Barium would probably act differently if fritted. In the raw state it does not seem reliable, though it enables the alumina to be reduced in amount.

The influence of silica is instructive. The addition of even a small amount to a matt glaze will brighten the surface, pointing to the probability that the matt texture is due to particles of alumina which have been rejected by the glaze composition, but which are siezed upon by the extra modicum of silica and brought into combination. This point will throw light upon the last question—the physical or chemical cause of the matt texture. In the first place it is certain that it is not caused by flotation. This is the difference between texture and scum. A good texture glaze is the same throughout its substance, the rejected particles are not thrown to the surface. Again, the texture is not due to immaturity. Some of these glazes have been fired to cone 9 without losing their quality.

I believe that the matt is caused by a disarrangement of the chemical relationship which exists between glaze constituents under normal conditions. While on the one hand an excess of acid may afford a texture by devitrification, which is only a name for the appearance caused by a rejection and separation of particles of silica, so, on similar but

opposing lines, another and different texture may be caused by an excess and consequent rejection of basic molecules.

The stability of the fired glazes has not been touched upon in this investigation. Some texture glazes are subject to decomposition from atmospheric influence, and they may be tested with acid vapors, but in the experiment undertaken here this has not been done.

DISCUSSION.

Mr. E. C. Stover: Mr. Walker, I will ask you whether, in the series of trials you made last year, you put through a series without color, in the various glazes included in your oxide of copper tests?

Mr. Walker: I did not. I don't think the small percentage of copper in my experiments would have had any appreciable effect. I think it would be found that the glaze without the copper would be very much the same as with it. I judge that, from looking at Professor Binns' trials which have been handed around.

Mr. Thomas Gray: Three or four weeks ago I had some matt glazes which I did not want. It was brought about by firing very rapidly with soft coal, only using about twelve hours start to finish. About one-half the kiln came out fairly good, but the rest was quite matt.

Mr. Karl Langenbeck: It seems to me hard to discuss such a paper, because it deals with matters of fact along a particular line, but a small part of the line being covered. Professor Orton recently conducted a line of experiments with glasses, and I think he could possibly throw some light upon the question, whether in an amorphous silicate, if the relations of alumina to silica are fixed within certain limits, the excess of alumina is thrown out and remains in the glaze; or whether, on the other hand, the limits are exceeded in point of silica and whether the silica is thrown out in a crystalline state?

The other question which comes up is the one indicated by the president, upon which Mr. Walker's immediate experiments do not seem to throw much light; but Mr. Grueby has stated to me that in his experiments, the cupric oxide

undoubtedly interfered with this behavior. The question is whether other oxides are substitutable for alumina?

Edward Orton, Jr.: We all feel the impossibility of giving anything like an adequate discussion of a paper like this. It simply emphasizes the fact that if we are going to do high grade work in the way of discussing papers, we must have them printed and sent to the members *in advance*, so we may be prepared to discuss them. No one can discuss a piece of work as painstaking as this, without giving it some study.

Regarding the experiments with glass to which reference has been made, I would say that they do not suggest anything in this connection, except the one fact that alumina does not always seem to assist in the production of mattness; but, on the other hand, may frequently powerfully assist in the production of glassiness. That principle was first stated by Mr. Langenbeck in his book, when he called attention to the difference between glasses and glazes, i. e., that in the glass, the ware is cooled so suddenly that no chance for devitrification is given, and alumina is therefore not needed and is, in fact, either low in amount or altogether absent, while in the glaze, it is only by the use of alumina that we can prevent devitrification during the long cooling in the kiln. I do not remember having seen elsewhere in ceramic literature this distinction so sharply drawn as Langenbeck made it there. One of my glasses produced last year showed this point beautifully. It was a series of glasses in which I had been persistently reducing the silica contents. I started with RO, 2.5 SiO_2, and reduced the SiO_2 one-half equivalent at a time to a very basic glass, RO, 0.5 SiO_2. The basic mixtures were not like glasses; they were more like stones. I then tried adding alumina to one of these same stony basic slags. The first addition reduced the stony condition greatly; the second produced a beautiful clear glass. In the third addition, the glass had gone beyond the point of maximum fusibility, and particles of white unfused matter were floating around in the clear matrix of the glass. Further additions of alumina made it stony again. There seemed to be a point where alumina made a stony basic slag into a perfect

glass, but also, it seemed equally clear that too much alumina converted the glass back to the stony condition again.

I value Professor Binns' paper very highly, and shall value it more as I have opportunity to study it. I have never done much experimenting along this exact line myself. I had one student who pursued the subject last summer for two months in a somewhat desultory fashion. He started to make a matt glaze, and attacked the problem from several different points of view. He first tried to determine whether mattness came easier from extremely basic or extremely acid glazes, and he came to the conclusion that it was easier to make a matt from the basic end of the series. The general formula of the glaze he finally reached was something not far from where Professor Binns wound up;—about thirty-five hundredths of alumina, and one and a half of silica. While this work was merely the work of a student, the same general ratio is borne out by his results.

The Chair: To what temperature did this student carry his experiments?

Professor Orton: Nought two.

The Chair: And Binns', nought one.

Mr. Thos. Gray: Series Four of Binns' trial-pieces seems to have a strong resemblance to the defective ware we got, and we decided a few days ago that more fire would be beneficial, and yesterday sent them to the kiln to be fired again. They seem to be much like one of these samples of Mr. Binns' We redipped a few, and they seemed to come out all right; so we sent the whole lot down yesterday to be fired again. The kiln was fired so rapidly on account of burning soft coal; our burners were not used to such a fuel and let the heat get away from them.

Mr. Karl Langenbeck: Of course it is possible that with the glaze having a tendency to devitrify if the conditions of firing were not closely maintained, devitrification of the glaze would explain the phenomenon you speak of. On the other hand, I have seen a raw glaze when fired with a very sulphurous coal, take on a slight scum of lead sulphate on the surface. I think a good many phenomena might look like this, and still come from very different causes.

I merely point out these differences, because I think it would be to the great interest of the members to get some kind of a classification of crystalline or amorphous separations from glass. In the first place, we need some nearer definition of glass than that of an amorphous silicate, which is very broad; then some information as to the kinds of separation which take place. There is such a phenomenon as the separation in crystalline form of an oxide which has supersaturated the glaze, as in crystals of chromic oxide in chrome aventurine. Also, there is the separation of sulphates from the glaze in crystalline form. There is the beautiful crystalline separations of which so much artistic use has been made recently by the Royal Copenhagen works, and again the separation of alumina in matt glazes. I should like to ask if anyone has made any observations on these lines, as to a possible classification?

Mr. Stanley G. Burt: I think a still further possible explanation of Mr. Gray's trouble is that the rapid firing may have brought about a reducing effect. If he had a certain per cent of lead in his glaze and had a smoky fire, he might have reduced it, and got a matt surface. He could then put it back in the kiln, and get it all right.

Mr. Gray: But, we have put it in again, without doing anything to it.

Mr. Burt: You re-oxidize it, by refiring it, and thus overcome the reduction of the first burn. I am a little disappointed that Professor Binns did not go into the crystalline structure of the matt glaze, and I agree with Mr. Langenbeck that it is a great field for study. We are undoubtedly getting at it more and more closely. The crystals of the Copenhagen ware are zinc crystals, as I know, and I also know of chromium crystals. The matt glazes which have come under my observation are almost invariably traceable to crystalline effect. I rather get from Mr. Binns' paper, tho it is a little hard to follow such a paper, that he has still in his mind some suggestion of suspension of alumina particles. To my mind, it is not a question of suspension purely, but more of crystallization; and in the study of the different glaze-crystals we arrive at the explanation of the different

grades of mattness. For instance, no one would call the Copenhagen glaze, however beautifully and completely crystallized, a matt glaze. Nor would you call a piece of the chrome-iron glaze, matt; nor would you call the Italian mosaic glass (aventurine) which is now made in New Jersey, I understand, a matt glaze. But, I feel that the matt glazes shown here by Professor Binns are very probably due to the fact that there are a number of bases all crystallizing out together, giving in that way a great mass of broken crystals together.

The Chair: Have any of the members had a chance to examine these samples of Professor Binns' under a high power glass.

Professor Edward Orton, Jr.: Some few of these crystals can be seen by the naked eye; but I think the crystalline formation of matt glazes must be proved by slicing and grinding, and then examining under a microscope, rather than by external appearance.

Mr. Karl Langenbeck: Some very interesting studies have recently been made on the crystallization of alloys of copper and aluminum; and the character of the alloys was brought out in a very interesting manner, by photographing the sections and projecting by means of a lantern on a screen. I think the suggestion is a very meaty one; and if some one having a connection with a minerologist who has a rock sectioning apparatus, is willing to prepare some of these for projection upon a screen, I think some very interesting things would appear.

Professor H. A. Wheeler: I think Mr. Burt's opinion of Mr. Gray's trouble is probably right. He likely had a reducing action. We also may have overlooked the fact that in glazes where there is a high percentage of alkaline earths, and the glaze is nearly saturated with them, letting the fires go up and down may result in crystalizing out. It is less likely to occur than the other explanations, but still that condition of affairs might arise in a kiln being burned by a careless burner, who did not keep his fires uniform.

Mr. Isaac Hardy: I understood Professor Binns to say that lead is indispensable to a matt glaze. The glaze I am

using to make what my firm calls satin-finish brick, consists of feldspar, flint, zinc oxide, calcium carbonate, and is burned up to cone six, and it will stand burning to cone ten and still give a matt finish. We take ten to twelve days to cool the kiln off. On some bodies, this glaze will come bright; on other bodies it will come matt; and again it will come semi-bright.

Professor Wheeler: Is you lime pretty high?

Mr. Hardy: I don't recollect just what it is. It is not very high—there is about forty per cent. of feldspar, I believe. If I had had copies of these papers beforehand I would have come prepared to discuss them. But as this is my first meeting, I did not know what line of proceedure would be followed, or I should have come fully prepared to talk.

Mr. Karl Langenbeck: The statements of the last speaker remind me of some experiments I made a number of years ago, starting with Seger cone four as a basis for hard-fire colored glazes. I recollect I substituted zinc oxide—small amount at that—for the lime, which in general would produce a glaze similar to what Mr. Hardy describes; and I got matt glazes then. And in connection with this matter, I particularly noticed in the glazes stained with oxide of manganese and oxide of copper, that the turbidity and texture of the matt glaze is more conspicuous than in any of the others.

Mr. Isaac Hardy: I do not get my matt finishes by the addition of alumina, but rather by the addition of silica. We have one glaze which comes quite bright, but by the addition of silica it changes to a matt finish.

Professor Orton: I think we all realize that mattness may proceed from a number of different causes. I think confusion has been brought about by considering lead glazes on the one hand, and another type of crystalline glazes on the other. They are not at all alike. In Bristol glazes such as Mr. Hardy and Mr. Langenbeck have just described, the effect may be reached by the addition of silica, while in lead glazes, it is reached by diminishing the silica. The same laws do not hold good for both kinds of mattness.

Mr. Karl Langenbeck: Is not the relation of alumina to silica a question of temperature? Say the firing is from cone nought five to cone nought one: in that case, starting with enough alumina to prevent devitrification, that is, the crystallizing out of the silica under long fire, the matt glaze would be produced by adding an excess of alumina. But in the case of a Bristol glaze, fired from cone six to eight or nine, while you have a large alumina content in comparison with the alumina content in the lead glaze, yet it is in all probability nearer to the devitrification point. If the proportion of alumina to silica is not high enough, a small increase in silica brings about the result mentioned. We must take temperature into consideration.

Mr. Alfred Yates: I will give a little experience I had in Johnsonburg. I had succeeded in getting a very bright glaze and I gave a copy of the receipt to a friend in New York. He put it on his body, and got a dull finish—the most beautiful glaze I ever saw. He used the same glaze, the same quantities of the ingredients, but used on two different bodies, the results were entirely different.

DEATH VALLEY, CALIFORNIA, AND ITS BORAX INDUSTRY.

By Edward Hart, Ph. D., Easton, Pa.

The Chair: Gentlemen, we are assembled here to listen to a lecture, illustrated by lantern views on the screen, by Professor Edward Hart, Professor of Chemistry at Lafayette College, Easton, Pa., and last year elected a member of this society. Many of you are acquainted with Professor Hart, by reputation if not personally, and those who have not had the pleasure of a personal acquaintance with him have missed one of the good people of the profession. We will now listen to Professor Hart. (Applause).

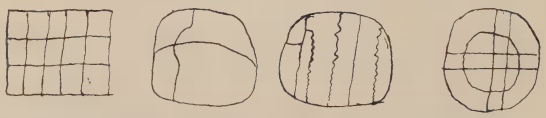
Dr. Hart: Gentlemen of the Ceramic Society.—For several years my friend Mr. Stover has been sending me every year about Christmas time some beautiful product of their factory at Trenton, and every time there has been a meeting of the Society, he has asked me for a paper. This year there was no present, and when Professor Orton asked me for a paper, I took the hint and will give you the best I have.

The country I am going to speak of is a very peculiar country. Before speaking of Death Valley, I shall take the liberty of saying a word about Adamana and the big trees there. While silica is one of the materials of the potter, it does not seem likely that we will ever be making commercial ware out of petrified trees. But as this discourse is only semi-scientific, I will bring it in on this pretense.

In all this southwestern country, the light is very strong due to the absence of moisture from the atmosphere, and, not being accustomed to photographing under such conditions, my pictures are all over exposed. On these deserts the surface soil has little or no covering, and the wind and rain have an excellent chance to play havoc. So it happens that while the rainfall is small, yet coming as it does in heavy downpours, it causes heavy erosion. The whole surface being ex-

PLATE 1

PLATE 2



INDIAN HIEROGLYPHICS NEAR SARATOGA SPRINGS.

(See Page 69.)

posed, anything that can be carried off by water is carried away; the water will carry nearly its own bulk of solid matter. The evidence of erosion is so great, that you would think the rainfall tremendous.

The first cut (see fig. 1) gives a good general idea of the appearance of the country. We visited a place near Adamana, where the ground was littered with pieces of tree trunks, which have in the course of many years been washed out of the mesas or table topped hills which abound. In the mesas, the trunks are found lying horizontally, and nearly unkroken, in a layer about fifteen feet from the surface, in a bed of what seems to be volcanic ash, below a capping of sandstone conglomerate. This sandstone seems to fall apart as the edge becomes exposed, probably under the influence of the frost, and is washed away. As the support below the trunks washes away unevenly, they break apart crosswise, never lengthwise, into sections of a foot to eight feet long. At one place (shown in the second cut) a trunk perhaps four feet in diameter and 120 feet long spans a ravine which has been excavated beneath it.

When we landed at Adamana, we found six inches of snow. I was determined to see the forest, however, even if I had to dig it out, and my determination was justified, for by the time we reached the forest we found the snow nearly melted off. On a rough guess I should think the trunks might cover about a thousand acres, the largest trunk I saw was about eight feet in diameter. There were no small branches—nothing less than three inches in diameter—and some of the trees showed evidence of decay before petrification began. I concluded, therefore that the trees must have fallen and the leaves and small twigs decayed before the silica solution which must have caused petrification began its work.

The driver informed us that there are four other petrified forests in the vicinity, one of them larger and finer than the one we saw. The forest we saw has been examined by experts in such matters who think the trees were Sequoias, but some pieces I saw, said to have been taken from the other forests, looked more like oak.

The accompanying rough sketch map will perhaps serve to give a good general idea of the country traveled over. It is a country of rough stony mountains and sandy valleys. The altitude at Daggett is about 2,000 feet and at Cave Wells about 4,000 feet. Death Valley is a little below sea level.

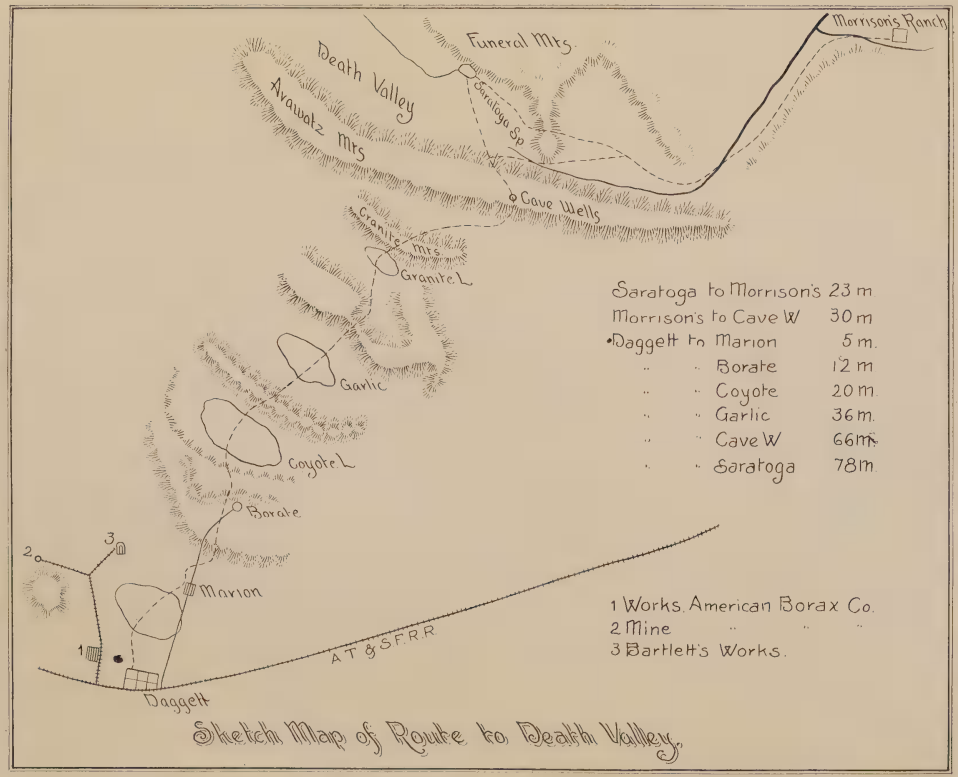
I arrived at Daggett on a Monday morning, at 5 o'clock, and found the town asleep. It is not an attractive looking place—no hotel, many saloons, and a general go-as-you-please look. I had hoped to be able to drop my title here but it was not to be. Eisenberg, one of our boys, had been at the borax works and some of the books we print at Easton were in their small library, so I was professor there too and after the first shock the people took it as well as could have been expected.

From here to Death Valley the trail runs in an almost straight line to the northwest, over several divides and across several playa lakes, gradually rising until it reaches the summit of the Avawatz Mountains. nearly 4,000 feet high, which border Death Valley on the south.

Daggett is situated on an open plain and is said to be on the bank of the Mohave River. To the uneducated eye the so-called river is nothing but a bed of sand. Like many of the streams in this arid land the river burrows in the sand and steals along next to bed rock beneath the surface. Dig there and you find water in abundance.

The trail from Daggett passes over the Mohave, then over a stretch of sand, and then over a playa lake to Marion, 5 miles. A railroad also runs to Marion, owned by the Pacific Borax Co.

These playa or dry lakes are a peculiar feature of this peculiar country. They contain for most of the year no water, the surface being fine, dry mud. The water from the surrounding country carries this fine mud during the infrequent downpours, and this is deposited as the water stands. Part of the water evaporates and the rest sinks below the surface, carrying with it most of the dissolved material. Very little evaporation takes place through this fine compact surface deposit. Most of it occurs at the edges of the lakes where the sand is coarser, and here the alkali crusts are to



Sketch Map of Route to Death Valley.

be found, Some of these playas are covered with cracks, others are almost entirely without them. They are perfectly level and the roads cross them in a straight line. When in good condition, as we found them, they make perfect roads, hard and smooth, and I believe one horse could pull 5 tons on such a road with ease. Coyote Lake was the largest lake we saw and is perhaps 5 miles in the shortest and 12 in the longest diameter. Many thousands of tons of alkali must be contained in the deposits around its edges and still more dissolved in the water beneath its surface.

At Marion the Pacific Borax Co. has built a mill for roasting the Colemanite. Colemanite is a borate of lime, containing water. On roasting, it loses the water and falls to a fine powder which can be sifted out. The valueless mud, mixed with some of the Colemanite, does not fall to a powder when heated and in this way the Colemanite is purified. The fine powder is put in sacks and sent to Bayonne, N. J., where it is treated with sulfuric acid which combines with the lime. The boric acid goes into solution in the hot water, which is poured off, and as this cools the boric acid crystallizes out. The boric acid is then sold as such for enameling iron, for pottery, for glass-making, etc., or it is boiled with carbonate of soda and so converted into borax. The Colemanite treated at Marion comes from Borate, 12 miles to the northwest of Daggett. From Borate to Marion it is carried on a narrow gauge road running along the trail. The grade is very heavy and the road crooked, crossing the trail repeatedly. As the engine comes shrieking around among the mud hills it looks like a veritable demon and frightens horses and driver. This country is full of boric acid, which seems to have accumulated in the ancient lake which once covered all this country, and has since completely dried up. At one place, 7 miles northwest of Daggett, an old lake deposit, 60-90 feet thick, is found standing now almost vertically. It is a hardened mud and was originally deposited as such on the old lake floor. It contains 10 per cent. of boric acid and is worked at Daggett, where it is mixed with water, treated with sulfur dioxid, made by burning sulfur, and the solution allowed to evaporate in shallow tanks. No artificial

heat is needed, the sun does the evaporating at a tremendous rate. This is easily understood. The temperature reaches 118 in the shade and there are frequent winds with a velocity of 40 miles and more an hour.

Most of the borax used in the United States comes from this little town of Daggett, where there are three producers. In 1901 we used a little over 18,000 tons of borax, of which probably nearly 17,000 tons came from Daggett.

My outfit for the trip to Death Valley consisted of a team of two horses, such as the horseman calls chunks, and a driver, known locally as Tug—a lad of 19. I paid $5 a day for the team and $3.50 to the driver. Food and water for ourselves and fodder for the horses we carried with us. We had also a mess kitt and our beds, but no tent. The bed is made as follows: First a strip of canvas 14 feet long and 5 feet wide is spread on the ground. On this is placed a mattress and pillow, on these a woollen blanket folded bag-fashion from the bottom. On this several blankets are placed and the canvas folded up over all. You find a level place, scrape away the stones, undress quickly, for the nights are cool, crawl inside and draw the canvas over the head. In the morning you dress, wash your face, if there is any water, and you are ready for the road. The bed is rolled up, tied with a rope and thrown on the wagon.

The amount of bread and butter eaten on this trip astonished me. Tug was no cook and I knew little more about it. We both loathed washing dishes, so that coffee and bread and butter formed our staple diet. We started out bravely with eggs and bacon, but to eat eggs and hog fat and then to clean that frying pan were too much for us, especially where water was scarce and time short. Our camp-fires were made of sage brush or grease wood. We tried cedar at one camp but did not like it. Sometimes it is hard to find wood enough to burn, and as for trees there are none—I saw nothing as thick as three inches.

We followed the trail used by the borax teams carrying supplies to their ranch in Death Valley, and crossed the playa lake to Marion, where we filled our canteens. Then to Borate and then to Coyote Well, on the border of the playa

PLATE 3.

1.—Fording the Amaragosa, looking north-west.
2.—Valley of the Armaragosa, looking west.
Avalvatz mountains in the distance.
3.—Sand Cliffs on the Amaragosa.

lake of the same name, where we watered our horses. Then on over a divide to Garlic, where we camped. This was thirty-six miles for the first day. Next day we pushed on over two divides to Cave Wells, in the Avawatz Mountains, where we watered the horses, and then to Saratoga Springs, which lies on the northern edge of Death Valley. From Cave Springs to the valley is a heavy grade down hill, 4,000 feet, and then across the alkali flats, perhaps two miles wide at this point. This day's journey was forty-two miles and the horses were very tired. Saratoga Springs bubble up at the very foot of the Funeral Mountains, which enclose the Valley on the north. The water is warm and contains some dissolved material, a little borax among other things. It is not very good for men, but horses can and do drink it. There are a few small fish in it and the puddles around it, called lakes here, are the resort of ducks and mud hens. Ten feet from the springs there is an alkali crust six inches thick. There is a small hay barn at Saratoga Springs where hay is kept for the borax teams. This hay comes from Morrison's Ranch. After supper I spread my bed on the hay bales inside while Tug spread his outside nearer the horses. About 8 o'clock we were roused by the noise of a team which turned out to be Morrison himself with a four-horse load of alfalfa, weighing 3,000 lbs. net, which he had hauled twenty-three miles from the ranch over very rough roads since 11 o'clock the same morning.

Next morning I climbed the mountains to look at the Indian hieroglyphics with which the rock are covered while the others were breaking camp. During the ride I visited, riding sometimes in one wagon and sometimes in the other. I looked upon Morrison with some curiosity. He has spent several summers here and told me that it was pretty hot sometimes—128° in the shade.

Until we reached Saratoga Springs our trail ran northeast. From there for about twelve miles it ran almost due east, crossing a low spur of the Funeral range with wonderful sand dunes lying on one flank in the distance, then crossing the Amaragosa river and curving to the north following the river. Up to the crossing of the Amaragosa, the

valley is very wide, but above that it contracts to a narrow canyon, hemmed in by walls of sand cemented together into a rock-like mass by alkali. A few miles below this crossing the Amaragosa, which has the volume of a small mill stream and contains much dissolved alkali, disappears under the sand.

Morrison's ranch, where we stopped that night, is on Willow Creek, about half a mile above its junction with the Amaragosa. The ranch contains about twelve acres under cultivation—mostly alfalfa—and is surrounded by clay hills in which nitrate of soda is found. The surface of these hills is like loose ashes for a depth of six to twelve inches. Below that a hard crust is found, containing the niter six to twelve inches thick and as hard as iron. In these hills and those lower down the valley, Bailey estimates the total amount of nitrate so far located as equal to 22,000,000 tons. At the present time, all our nitrate for making gunpowder, nitric acid, gun cotton, nitroglycerin and celluloid comes from Chile.

We imported in 1901 233,720 tons nitrate of soda from Chile, so that at the present rate of consumption these California deposits contain enough to supply our wants for nearly 100 years.

Within a short time a new railroad from Salt Lake to Los Angeles will cross this valley and then these salt deposits can find their way to market. On the way to Morrison's we met a party of twenty-five prospectors belonging to the American Nitrate Company, and at the ranch we found as many more encamped. At the head of the party was Mr. Norton, who goodnaturedly offered to loan me his bed, which I declined with many thanks. Next morning bright and early we left for home, going back over our route out for most of the distance. On the way Tug discovered a tarantula, who had been out too late and been overtaken by the cold night air and benumbed, and I took his picture. Tug said that when he was smaller, one of the Daggett doctors bought tarantulas for four bits, or fifty cents each, and the boys caught them as follows: The tarantula burrows in the sand, with a trap-door closing his hole two inches from the sur-

PLATE 4.

1.—The Amaragosa River, sinking into the sand.
2.—Sand Cliff on the Armaragosa.
3.—Morrison's Ranch, Nitrate Hills In background.

face. One boy creates a disturbance around the door and the tarantula rushes up, closes it and holds on, then the other boy inserts a shovel below him and throws him out on the sand, when he is quickly caught in an empty bottle.

The first day of our return journey was Christmas day. In the morning it was cold, but by noon the temperature was at 80°. We had bread and butter and canned salmon for dinner, and for dessert I prospected and found a gypsum deposit, while Tug smoked cigarettes.

That night we slept at Cave Wells. The rocks here are infested with rats, and they held high carnival, running back and forth over our beds. In the summer this must be a lively place. Tarantulas are plentiful, and there is a snake which Tug called a "side winder"—poisonous.

Next day we reached Coyote Wells on our return, forty-six miles—our longest day's journey. On the way we met and passed the borax team taking supplies to the ranch. There were twelve mules and two lead horses. In the old days, twenty mules pulled two wagons hitched tandem, the mules two abreast. These wagons could carry, besides supplies and water, 52,000 pounds. Such a team travels about twenty miles daily. The cost of freighting in the desert is about twenty cents per ton mile. Next morning it was very windy. Breakfast was gotten ready under difficulties, and the wind was very strong for several hours. Then it moderated and we rode into Daggett at high noon, tired, hungry, and dirty. I was very much indebted then to Mr. Henry Blumenberg, superintendent of the American Borax Company, for he added to much previous kindness, the loan of his bath-tub, one of a very few—perhaps the only one in Daggett.

Next morning at 3 o'clock I boarded the train and at the Harvey eating house, at Los Angeles, gorged on dainties and rejoiced that I need not live in Death Valley.

DISCUSSION.

Mr. Karl Langenbeck: What is the nature of the soluble salts, in the sand banks on the Amaragosa?

Dr. Hart: I do not know of my own knowledge. None of my samples have come to hand. Bailey's report, which

treats of the matter pretty fully, states that they vary in composition. Salt is a prominent constituent. There is sulphate of soda there, carbonate of soda in places, tho not much, I think. These seem to be mixed up in varying proportions. On the sides of the wash, leading out of the Valley, are salt deposits of considerable extent. There is plenty of gypsum there, too. But the whole country seems to be liberally scattered over with these materials, and it looked as tho it had been thoroughly stirred afterward.

The nitrate deposits are covered by claims, bought up by the American Nitrate Company, which will soon be operated. A new line is to be run from Salt Lake City to Los Angeles. It will cross this country about midway between the different nitrate deposits, which it will be possible to reach by narrow guage roads from the main line.

Mr. Langenbeck: By nitrate, you mean nitrate of soda?

Dr. Hart: Yes.

Professor Edward Orton, Jr.: Where do they get the water supply for leaching out these beds?

Dr. Hart: There is nothing of that kind done in the Valley now. No practical work, nothing except prospecting, has been done in the Valley except the hauling of Colemanite to Mojave. We found a prospecting party of about fifty people belonging to the American Nitrate Company, and there were several parties from the Pacific Borax Company in the field, but no practical work is being done. The factories are at Marion and at Daggett. The American Borax Company is at Daggett.

Mr. Langenbeck: All the borax at present made comes from these borax deposits?

Dr. Hart: Yes. The Colemanite mines of the Pacific Borax Company are at Borate, about twelve miles from Marion. The Boric acid made at the Bartlett works is made from the borax mud deposits of that region. The American Borax Company's mine lies about seven miles from Daggett, connected by a narrow guage road. The ore is brought to Daggett and there turned into boric acid. The water at Daggett comes from the Mojave river. The river there is

under the sand. They sunk wells, found the river and have plenty of water.

Mr. Stanley Burt: The refining is completed right there? Do we receive it direct from there?

Dr. Hart: Boracic acid is shipped from there mostly to Pittsburg. But the American Borax Company's work is so far only in the experimental stage. Mr. Blumenberg told me he had a three month's run last summer, and found what he could do, and is now going ahead on the basis of that.

Mr. Langenbeck: Mr. Burt's question is of interest to users of boracic acid for ceramic purposes. It has transpired that there is a good deal of sulphate of ammonia in some boracic acid of Italian origin, which has caused disagreeable results.

Dr. Hart: Yes. Ammonia occurs as a sulphate in the Italian deposits. I have no knowledge of such impurity in the California borax; the samples I secured there have not yet come to hand, and so I have not been able to make any analysis yet.

Professor Orton: Is there any animal life there, to speak of?

Dr. Hart: My driver told me that in the summer time it is quite interesting. The tarantulas at Cave Wells are very thick, and it is difficult to find a place not already preempted. The night I was there, the rats or mice had a jamboree, and raced across my bed a number of times. I think probably in the summer time there is a good deal of life. I saw nothing but a few mud hens, a single tarantula, and I think three chipmunk and a lizzard which came out in the middle of the day. But there is evidence there of a swarming animal life in the summer time.

Professor Orton: I move that the Society express its gratitude to Dr. Hart for the exceedingly interesting lecture he has given and for the care and trouble he has taken in preparing it for us by a vote of thanks.

Motion seconded. and unanimously adopted.

RECENT INVESTIGATIONS IN PORTLAND CEMENT.*

BY ALBERT V. BLEININGER, B. SC.

It is a difficult task to collect the experimental data produced by the many investigators who have worked on the examination of the hydraulic silicates and especially of Portland cement. Keen scientific minds, equipped with thorough training, have applied their energy to the solution of the various problems connected with the Portland cement industry. As a result, we have before us a mass of material representing an enormous amount of work and energy, and differing widely in scientific value; the investigation of the thoroughly equipped chemist and mineralogist is found in the various journals, side by side with the speculations of the obscure and often untrained observer. In addition, these multitudinous results are found scattered in many different periodicals in three or four languages. If, in attempting to produce an outline of the work recently done in this direction, the task is not complete, it is due to the great amount of material in existence, and to the fact that it is scattered over such a wide territory.

It is a peculiar fact that the great bulk of the work in the investigation of Portland cement has been done along theoretical lines, as distinguished from similar work done by the metallurgists on steel, where the first problems attacked were strictly practical in character, and have only of late developed a phase which might be said to be strictly scientific, almost entirely freed from empiricism. The investigation of the true character of Portland cement seems to have had a great fascination for the very first observers.

Since Vicat (1857) Candlot, Fuchs, Feichtinger, many experimentors have endeavored to arrive at results, which might throw light on the vexed question of the constitution of cements with but indifferent results, since most of them endeavor to make use of wet reactions. All of them found

*Published in advance, by permission of Edward Orton Jr., State Geologist of Ohio.

that the calcareous cement compounds are extremely unstable. Michaelis, in the sixties, has shown that even alcoholic solutions of salts in the absence of water decompose the hydraulic compounds. Up to about 1887, all that was known concerning the hydraulic cements might be summed up in a few sentences, viz:

Natural or artificially prepared mixtures of silica, alumina and carbonate of calcium, when heated above redness, produce compounds which harden in contact with water. The hydraulic compounds produced are calcium silicates and perhaps aluminates, which unite with water, chemically, giving rise to a mixture of hydrous salts.

It is not until the aid of the microscope was called in (1887), that more definite statements could be made, although all this while, the gross composition necessary for a good Portland cement was known.

In this year Chatelier[1] published his classical work on the constitution of Portland cement, based on microscopic analysis, in which he states that he found the main constituents of Portland cement to consist of, (1) colorless double-refracting, cubical crystals; (2) between these a darker substance, double-refracting, but without crystalline structure. In addition, he found several accessory constituents,

(a) slightly yellowish crystals, opaque and showing striation,

(b) very small crystals with rather strong double-refraction, and

(c) finally zones of matter without influence on polarized light.

Constituent No. 1 was called, later, alite; No. 2, celite; a, belite; and, b, felite. Chatelier considers the alite as $3\ CaO\ SiO_2$, this being the active element of cements, par excellence, which hydrates according to the following reaction:

$$3\ CaO\ SiO_2 + Aq = CaO\ SiO_2\ 2.5\ H_2O + 2\ Ca\ (OH)_2.$$

In addition to this compound, the Portland cement contains a tri-calcic aluminate, which is relatively unsta-

1 Recherches experimentales sur la constitution des mortiers hydrauliques. Annales des Mines 1887.

ble, but sets rapidly in water, and if present in too large amounts, may cause the destruction of the cement. It hydrates according to the reaction:

$$3\ CaO\ Al_2O_3 + Aq = 3\ CaO\ Al_2O_3\ 12H_2O.$$

Chatelier thus considers Portland cement as composed of tri-calcium silicate, with a certain amount of calcium aluminate and ferrate, besides mono-and di-calcium silicates. The hydration of the cement he expresses by the two reactions:

$$2\ (3\ CaO\ SiO_2) + 9\ H_2O = 2\ CaO\ SiO_2\ 5\ H_2O + 4\ Ca\ (OH)_2.$$

Then a reaction takes place between the calcium hydrate, water and calcium aluminate forming a basic calcium aluminate:

$$3\ CaO\ Al_2O_3 + Ca\ (OH)_2 + 11\ H_2O = 4\ CaO\ Al_2O_3\ 12\ H_2O.$$

The hydrated basic aluminate determines the setting of the cement, while the hardening is fixed by the tri-calcium silicate. Chatelier fixes the amount of lime necessary for Portland cement by the expression:—

$$\frac{CaO}{SiO_2 - Al_2O_3 - Fe_2O_3} > 3$$

in which CaO, SiO_2, $Al_2\ O_3$, $Fe_2\ O_3$ represent the number of equivalents of these substances present. The other limit he fixes by the expression:—

$$\frac{CaO}{SiO_2 + Al_2O_3 - Fe_2O_3} < 3$$

Toernebohm checked the petrographic work of Chatelier, but did not agree with the latter as to the composition of the tri-calcic silicate.

W. B. and S. B. Newberry[1] agreed in the main with Chatelier's results, but took exception to his tri-calcic aluminate, which they replaced by bi-calcium aluminate, so that they obtained the formula:—

$$X\ (3\ CaO\ SiO_2) + Y\ (2\ CaO\ R_2O_3.)$$

Dr Tomei[2] treated hardened cement with an aqueous solution of ammonium chloride and found that the amount of lime dissolved decreased after some time. He concluded from his experiments that the stability of the lime compounds increases with the time and that part of the silica

1 Journal of Society for Chemical Industry, 1897.
2 Thonindustrie Zeitung 1895, page 177.

from the sand of the mortar, enters into combination with the lime.

In 1895, A. Hauenschild[1] treated a number of hydraulic cements with various solutions of ammonium salts and found that these salts did not permit of an exact determination of the lime compounds.

The work of Toernebohm and Newberry was condensed by Meyer (1896) in the formula:—

$$X\ (3\ CaO\ SiO_2) + Y\ (5\ CaO\ R_2O_3\ SiO_2)$$

This investigator objected to the assumption of aluminates and ferrates, since alumina and ferric oxide always form a double silicate in the presence of lime.

Microscopic examination in no case showed the presence of free lime.

Prof. Rebuffat,[2] of the University of Naples, in 1898, divides cement, into two classes:

1. Cements of simple, compact structure, non-crystalline, derived from a mixture of calcium oxide, silicate, and aluminate. The calcium oxide may be absent. These comprise the hydraulic limes and quick setting cements.

2. Cements of crystalline structure derived from a combination of a crystalline mass, consisting of 2 $CaO\ SiO_2$ and CaO and the calcium aluminate in various proportions—Portland cements and cements high in silica.

He assumes that the qualitative constitution of the different hydraulic cements after setting is the same. They are formed from a mixture of lime hydrate, hydrated calcium silicate and hydrate calcium aluminates with a slight quantity of accessory ingredients. The calcium silicate is the ortho-silicate—2 $CaO\ SiO_2$. The quantity of the water of hydration which is absorbed does not exceed $5\frac{1}{2}$ per cent. so that the hydrated compound has the formula 2 $CaO\ SiO_2 + H_2O$. In cements high in silica, the presence of a certain quantity of meta-silicate must be accepted. This does not hydrate, but reacts with the aluminates and forms double silicates of calcium and alumina. This fact is important, as it explains the resistance of cements to sea water.

1 Thonindustrie Zeitung 1895, page 239.
2 Gaz. Chim. Ital. 1898.

The calcium aluminate may have one of the following formula:—

$$CaO\ Al_2O_3.$$
$$2\ CaO\ Al_2O_3.$$
$$3\ CaO\ Al_2O_3.$$

But unless there is an excess of lime or unless certain conditions of burning prevail, it seems that only $CaO\ Al_2O_3$ and $2\ CaO\ Al_2O_3$ should be considered.

The quantity of water chemically fixed by hydration cannot be determined beforehand. The cements hydrate in different degrees, according to whether they harden in pure or lime water. To this are due many peculiarities in setting.

In setting, the calcium ortho-silicate is hydrated to form $2\ CaO\ SiO_2 + H_2O$, which is followed by the hydration of the calcium aluminate. These two reactions take place in different phases for different cements.

With cements of crystalline structure, it must be assumed that the calcium ortho-silicate is found combined with CaO and the calcium aluminate in a definite crystalline condition. Portland cement in the hydrated condition contains but small quantities of calcium aluminate. This explains that in cements of crystalline character the setting may be caused by the hydration of the calcium ortho-silicate according to the following reaction:

$$2\ (3\ CaO\ SiO_2) + 3\ H_2O = 2\ (2\ CaO\ SiO_2)\ H_2O + 2\ Ca\ (OH)_2$$

This reaction is associated with the hydration of the aluminate, which in Portland cement consists mainly of mono-calcium aluminate and hydrates with seven molecules of water.

$$CaO\ Al_2\ O_3 + 7\ H_2\ O = Al_2\ O_3\ CaO\ 7\ H_2\ O$$

Rebuffat found that all the water of crystallization does not become free at low heat, but part is expelled at a bright red heat.

Prof. Rebuffat's work rests on the assumption that the free calcium oxide can be removed from a cement by means of a sugar solution of certain strength, an assumption which has not been verified by the work of Michaelis and Feret[1] who throw strong doubts on this method.

1 Internat. Congress for testing building material, Paris, 1900.

Michaelis in 1892 and Erdmenger in 1893, have shown that the bi-calcium silicate in a cement gives rise to "dusting," that is, it breaks down to a powder without showing hydraulic properties. This is supported by the later work of Newberry. Hence, cements low in lime or such whose silica content is enriched by the silica from the ash of the coal will show this disastrous behavior. But from further experiments, Erdmenger came to the conclusion that there must be an allotropic modification of the bi-silicate, since the same cement low in lime when cooled suddenly by quenching in cold water did not dust. The same change from one state of the bi-silicate to the other is determined by the length and intensity of burning. As soon, however, as more lime is drawn into reaction and the cement approaches the empirical tri-calcium silicate composition, the phenomenon of dusting disappears.

In 1898 Prof. Carl Zulkowsky,[1] of the University of Prague, also published his results on the investigation of cements. He believed that he could remove the free lime from cements indirectly, by using dilute hydrochloric acid. His main argument, however, is based on the study of blast furnace slags. His conclusions are summarized as follows:

I. The blast furnace slags, suitable for the manufacture of cement are highly basic meta-silicates whose decomposition is prevented by rapid cooling—granulation.

II. Owing to their anhydrous condition they have a tendency to unite with water and to harden, which is assisted by the presence of alkalies. Such silicates may be called hydraulites.

III. On slow cooling an inter-molecular decomposition of the meta-silicate or hydraulite takes place in a greater or smaller measure. During this process the mass loses its uniformity and the constituents are not dissolved by weak acetic acid in the proportion in which they are present in the slag.

IV. The hydration of the powdered basic meta-silicate is co-incident with a change in volume and a change in the

1 Die Chemische Industrie 1898, page 69.

shape of the grains which now fill all the space and gradually harden to a compact mass.

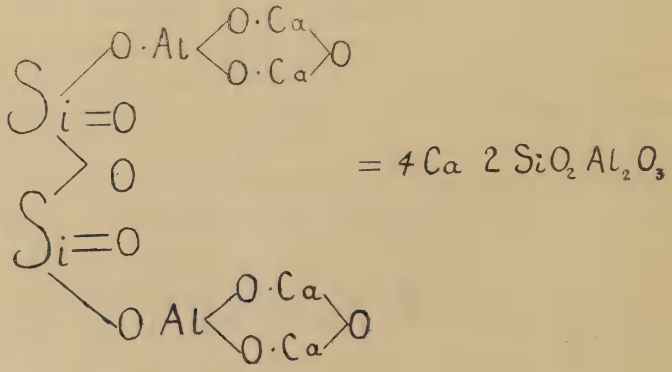
V. Slags cooled slowly, which contain only certain components or isomeric compounds of the above meta-silicates, do not possess the properties of the hydraulite, mentioned under II and IV.

VI. Portland cement, like slag cement, is a mixture of a hydraulite analogous to granulated furnace slag and with as much lime as remained uncombined on burning. The difference between the two is only that the necessary lime must be added to the slag in the shape of calcium hydrate.

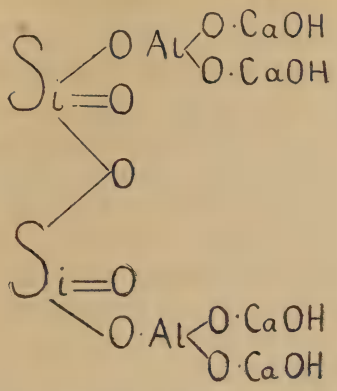
VII. The CaO of Portland cement cannot be separated directly.

VIII. The calcium oxide may, however, be removed from Portland cement by a special treatment with dilute hydrochloric acid in greater or smaller amounts, and the hydraulic property is diminished accordingly. The residue remaining behaves like highly basic slag; that is, it hardens in the presence of the alkaline compounds without combining with them chemically.

IX. But since the calcium oxide is thus removed in the wet way, the cement is sufficiently hydrated and the residual cement can never attain its original strength. The hydraulic agent of Zulkowsky is represented by the structural formula:—



This compound hydrates to:—



This formula is thus seen to be deduced from a basic meta-silicate which hydrates by the taking up of a molecule of water.

In 1899 Dr. Michaelis[1] published a startling theory which contradicted all the previous assumptions. He claimed that the hydraulic hardening is a combination of chemical and physical processes. For the main constituent, the hydro-silicate of lime crystallization cannot be proven notwithstanding the claims of Chatelier and others. The process of hardening depends upon an increase in volume on the part of some of its constituents, or the formation of gelatinous silicic acid. On letting a large quantity of water act on Portland cement, the volume of the latter is changed to a colloid mass occupying 33 times the original volume. On treating cement with lime water, the volume is increased 21 times. Even quartz, when treated with milk of lime, is converted into the colloid variety in which it is greatly increased in volume. The same is true of alumina and iron. Michaelis cites the manufacture of sand brick, by the action of calcium hydrate on crystalline silica as a proof of his theory. His claims, however, have found no approval by most of the cement chemists and investigators.

In 1897 Liamin,[2] a Russian investigator, made an extensive investigation of Portland cement by means of micro-

1Thonindustrie Zeitung 1899, page 785.
2Report of the Imperial Russian Technical Society 1897.

scopic examination, physical separation and chemical analysis. He made photographs of micro sections of hardened Portland cement, in which he showed the crystals of calcium hydrate. By means of a suspension method employing heavy liquids like methyl iodide and benzol, he washed out the calcium hydrate from the finely ground cement. This work he attempted to check by the determination of the combined water in the hardened cements, assuming that the hydrous lime silicates lose their combined water at about 160° C, while the calcium hydroxide loses its chemical water at from 450-480° C. In this way, he calculated the amount of calcium hydrate present by a very ingenious method of reasoning. These results apparently checked beautifully with the values obtained by the physical separation. In five Portland cements, he found up to 33.6 per cent. of calcium hydrate. The hardening, he claims, is due to the interlacing of crystals of lime hydrate and a lime alumina silicate. The important factor is the calcium hydrate, which he found in crystals about one millimeter long. Roman cements do not show this phenomenon to any extent. The content of calcium hydrate increases slowly since the higher calcium silicates gradually change to simpler compounds and lime hydrate. Thus the 3 CaO SiO_2 of Chatelier is reduced to the simple CaO SiO_2 occurring as fine, hair-like crystals, and hexagonal crystals of Ca (O H)$_2$.

Many investigators object to this extraordinary high content of calcium hydroxide and it has been shown by work done by the Ohio Geological Survey that the dehydration of cement is not as sharp and smooth a process as accepted by Liamin and that hence his dehydration values are erroneous. The last traces of combined water are expelled only at a red heat.

In 1899 a great number of experiments were made to determine the free lime in Portland cement for all investigators realize that if once it is possible to determine the free calcium oxide, the entire question of cement constitution is solved.

B. Steuer[1] allowed hydrogen sulphide to act upon water in which finely powdered Portland cement had been poured. In this manner, he extracted 44 per cent. of calcium oxide which he considered free lime while the residue corresponded to the formula $CaO\ SiO_2$.

S. Wormser and O. Spanjer[2] used as reagent for the solution of free lime, an alcoholic solution of aluminum chloride. They claimed to have proven that this solution (1 g in 100 cc's. absolute alcohol) does not decompose the silicates, but dissolves only free lime. The per cent. of CaO found to go in solution as such was 25, while in addition 20 per cent. of lime was found present as a highly basic silicate. They calculated by means of their method, a content of 26.6 per cent. of free lime, and 18.65 per cent. of CaO, combined with 6.15 per cent. silica.

Dr. Hart[3] in the same year, by means of a 10 per cent. alcoholic iodine solution found, he claims, 30.34 per cent. of free vitrified calcium oxide in Portland cement; the balance of the cement material he considers as ballast, a slag which does not harden; on hydrating, this vitrified lime hardens under water. He cites this free lime as a fine example of a body whose chemical energy is manifested, not by a thermal reaction, but by a mechanical development of energy. The reason why so much free calcium oxide is not injurious to the cement, he explains by saying that this lime is vitrified and crystalline. Vitrified, crystalline calcium oxide and the amorphous lime, though not distinguished analytically, are different physically. This argument is open to many objections, whose discussion here would lead too far.

Dr. Hart's work was supported, however, by thermochemical experiments, in which he determined the heats of neutralization of Wollastonite $CaO\ SiO_2$, artificial $CaO\ SiO_2$, $2\ CaO\ SiO_2$, $3\ CaO\ SiO_2$, $CaO\text{-}Al_2O_3$, $2\ CaO\ Al_2O_3$, $3\ CaO\ Al_2O_3$. He determined the heats evolved for the anhydrous cement as well as for the hydrated and dehyd-

1. Thonindustrie Zeitung 1899, page 604.
2. Ibid, page 1785.
3. Ibid, pages 659, 770, 853, 1569; 1900, page 188.

rated cement which had been allowed to harden. The heat of neutralization of the hardened, not dehydrated cement should be higher than that of the clinker, since the former contains a considerable amount of free calcium hydrate. In Portland cement the heat of neutralization is lowered on hydration, while the heat evolved by the dehydrated cement is almost equal to that of the clinker. From this Dr. Hart concludes that from 30 to 34 per cent. of free lime must be present in cement.

Dr. Michaelis objected to the use of wet reagents for the determination of free lime, claiming that they cause grave inaccuracies.

Dr. Wegner[1] allowed carbon di-oxide to act upon cement at a red heat, in a furnace fired by gasoline. He attempted to determine the free lime by this method and found 11 per cent. of CaO. This work obviously is of but little value since a constant temperature of 800° C is required, which cannot be said to have existed in his furnace, and to be of value, the experiments should have been conducted in an electric furnace.

Wormser[2] studied the reaction of ammonium oxalate on calcium aluminates and silicates, as well as on Portland cement at a red heat. He claims to have found the composition of Portland cement to be:

14 per cent. $CaO\ Si\ O_2$
43 per cent. $2\ CaO\ Si\ O_2$
23 per cent. $2\ CaO\ Al_2\ O_3$
20 per cent. CaO.

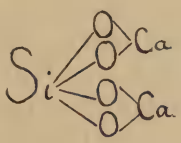
In 1901 A. Meyer[3] published his interesting account on the formation of cement, in which he summarizes his theoretical and practical experience. First a mono- and bi-silicate of calcium is formed, followed by the formation of an aluminate and ferrate of lime; then a tri-calcium silicate is formed accompanied by the crystallization of the stable double-silicate of lime and alumina. After the formation of the tri-calcic silicate, only bi-silicates can be produced. Be-

1. Transactions Society German Portland Cement Manufacturers 1901.
2. Ibid.
3. Bull d. l. Socite des Sciences de Boucarest 1901, No. 6.

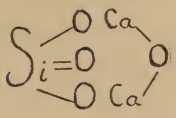
side this, an isotropic lime-alumina-silicate may be formed. The time of burning and cooling is of great importance on the reaction. The more basic the mixture, the less fusible will it be; hence, the higher the required temperature. A normal cement may dust if heated too long, while if burnt rapidly, it will show the proper behavior. If the amount of bi-silicate is too great, the cement will dust; this formation of bi-silicate can be prevented by rapid cooling. In many well burnt Portland cements, the main mass is a devitrified glass, in which several minerals in well developed crystals are observed.

A basic furnace slag, granulated, does not represent a devitrified glass, but a true bi-calcium silicate and aluminium silicate.

Everything tends to show that the bi-calcium silicate may exist in two forms:

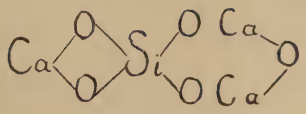
Ortho Silicate 

and

Meta Silicate 

The latter hydrates, since it contains the lime as anhydride. If exposed to a higher temperature, it changes to the crystallized ortho-silicate, which falls to a powder. In cooling blast furnace slag rapidly, we retain the meta-silicate, thus preventing the change to the ortho-silicate.

In Portland cement, which is not granulated, the formation of the non-hydraulic bi-calcium silicate is prevented by adding so much lime that the tri-calcium silicate is produced:



In this, two-thirds of the lime is hydrated. But, so far, nobody has succeeded in producing the tri-calcium silicate by direct synthesis. Newberry could not have had it, owing to the imperfect mixture of the ingredients used, and to the lack of all analytical data regarding it; Rebuffat produced a mixture of less basic silicates and free CaO. Chatelier produced it indirectly with the use of fusing calcium chloride.

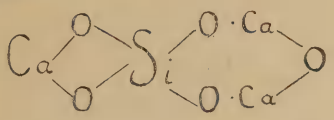
Edward Jex[1] in 1900 claims that the ortho-calcium silicate must be the main hydraulic agent of Portland cements. A meta-silicate is always produced by fusing a cement mixture, and an ortho-silicate can arise only in vitrification when greater resistance is offered to the motion of the molecules, so that each molecule is surrounded by several molecules of calcium oxide. If the clinker is heated for a longer time, the ortho-silicate reverts to the meta-silicate and hence the quality of the clinker is lowered. This difficulty is overcome by introducing more lime than is necessary for the ortho-silicate. This is a purely mechanical but good means of preventing the meta-silicate formation. But it is doubtful whether it would not be better to be rid of this excessive amount of lime. According to this investigator, the resulting compound in cement would be :

$$2\,CaO\,SiO_2 + 2\,CaO\,Al_2O_3$$

The dusting of clinker he explains by the presence of a mixture of meta- and ortho-silicate, which possess a different constitution, tending to break up the mass. Jex also suggests the possibility of producing a Portland cement by fusion, in kilns similar to a blast furnace. The raw material could be introduced in the shape of crushed rock, while the cement mixture is discharged in the liquid condition and granulated. The fuel consumed would be about 1 .5 times the amount used in the rotary kiln, but the process would do away with the power consumed in the fine grinding of the raw mixture.

1 Thonindustrie Zeitung 1900, Nos. 133, 136, 139.

In 1901 Th. Ludwig[1] compares cements with glasses, which might be called alloys. It is his opinion that the formula of A. Meyer:



represents the proper chemical conception of one of the glass constituents, the alite, which may crystallize out, though he denies that any experimentor has ever produced this silicate in the pure condition. He also supports Meyer's formula:

$$X\ (3\ CaO\ SiO_2) + Y\ (5\ CaO,\ R_2\ O_3\ SiO_2.)$$

replacing the modified Chatelier formula:

$$X\ (3\ CaO,\ SiO_2) + Y\ (2\ CaO\ Al_2\ O_3).$$

He doubts the presence of ferric silicate, claiming that the iron is always present as ferrous oxide.

This has been disproved by Loebell, and by work done by the writer for the Ohio Geological Survey, in which the iron was found in several cements to be largely in the ferric condition.

In the same year, Dr. Rohland examined Portland cement from the stand-point of hydrolysis, but arrived at no definite conclusions.

In 1901 Zulkowsky[2] again published a most valuable series of experiments whose results may be summarized as follows:

The existence of the tri-calcium silicate is not probable and not proven. The di-calcium meta-silicate is the true carrier of hydraulicity, which means the presence of free calcium oxide. (He could not produce the tri-calcium silicate, but did not use fluxes). Silica with a valence of six does not exist. The tri-calcium silicate is not necessary for the production of a good Portland cement; in fact, Zulkowsky produced a high grade white Portland cement of the formula 2 CaO SiO_2, 2 CaO $Al_2\ O_3$ from kaolin. Any lime above this is unneces-

1 Thonindustrie Zeitung 1901, No. 142.
2 Zeitschrift fur Chemische Industrie p. 290.

sary. He compares Portland cement with an alloy, in which CaO is in solution. Hence there might be a distinction between alloyed and unalloyed lime, which will slake in different ways. In presence of an excess of calcium oxide, the cement contains dead-burnt and alloyed lime. It is nearly certain that the first will slake like the hydraulites, the second much later, like dead-burnt lime, giving rise to "blowing."

In 1902 Rebuffat[1] gives an elaborate account of his latest studies, in which he pays special attention to the rapid-setting cements of the type of the natural cements. He started to produce these cements synthetically by the use of kaolin and calcium carbonate, heating them to about 800° C. In this connection, he found the remarkable fact that crystalline calcium carbonate, or even lime hydrate, when ground together with kaolin and burnt, did not give rise to hydraulic cements at all. After experimenting for a considerable time, he found that neither of the above forms of lime reacted sufficiently, and subsequently he was compelled to use amorphous calcium carbonate, precipitated by ammonium carbonate. The crystalline calcium carbonate reacts only at higher temperatures. By using amorphous calcium carbonate, he obtained synthetic cements, with kaolin, which showed satisfactory behavior.

This work of Rebuffat agrees with the work of the writer done for the Ohio Geological Survey in 1902, up to a temperature of 1100° C, at which point, crystalline calcium carbonate was found to react with mixtures of kaolin and flint, producing hydraulic cements equal in strength to the natural cements. There is no doubt, however, that amorphous calcium carbonate would increase the strength attained considerably. Rebuffat found that free silica is not necessary in the production of hydraulic rapid-setting cements, as mixtures of kaolin with 3, 4, 5, 6 and 7 molecules of calcium-oxide give very quick setting cements—the most rapid one being, one molecule of kaolin to six molecules of CaO, burnt at 800° C.

1 Thonindustrie Zeitung No. 105.

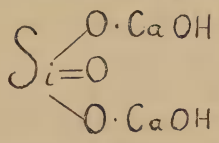
Rebuffat also treated all of his cement mixtures with sugar solution, by means of which he expected to extract the lime and he determined the chemically combined water of the various lime compounds. Rebuffat's synthetic work may be summed up as follows:

On heating mixtures of kaolin and calcium carbonate from 800 to 1200° C, the change in the time of setting is equivalent to a change in chemical reaction, as indicated by the increasing amounts of chemically combined water. The pozzulanic character of the natural cements is due to the presence of clay substance, and not to the free silica.

Rebuffat extended his experiments to natural rock cements, and arrived at the following conclusions:

Natural cements contain amorphous calcium carbonate. A synthetical mixture of SiO_2, Al_2O_3, and amorphous calcium carbonate, does not produce a rapidly setting cement. A mixture of previously prepared silicates and aluminates is not hydraulic at 800°, hence the natural cements are not mixtures of silicates and aluminates. All facts tend to show that natural cements are lime-alumina silicates, which above 800° gradually change to a mixture of calcium silicate and calcium aluminate; a change completed at 1200° C. If the mixture contains so much lime that all of the alumina becomes bi-calcium aluminate, the product at 1200° may retain a certain rapidity of setting.

A. Meyer[1] in 1902 reports the production of tri-calcic silicate from a fused magma, which hydrated to $2\,CaO\ SiO_2\ H_2O$; at 160° C, half of the fixed water is expelled, which indicates that the molecule must be a double one. The remaining water leaves at a much higher temperature than 200°. Hence it is impossible to have a meta-silicate—



for here the two hydroxides are united with lime and behave analogous to calcium hydrate, which loses its water at a much higher temperature.

1 Thonindustrie Zeitung No. 144.

The hydration equation of the main constituents of Portland cement can be said to be:—

1. $2\,(3\,CaO, SiO_2) + Aq = 2\,(2\,CaO\,SiO_2\,H_2O) + 2\,Ca\,(OH)_2$

2. By washing out the calcium hydrate the reaction can be carried to the following limit:—

$2\,(2\,CaO\,SiO_2\,H_2O) + Aq = CaO\,2\,SiO_2\,3\,H_2O + 3\,Ca\,(OH)_2$

The presence of a tri-calcic silicate is more readily to be assumed than that of meta-bi-calcium silicate and excess of lime. The alumina and lime are firmly united with SiO_2 and hence there are present no aluminates or ferrates.

In 1902 N. Liamin[1] investigated the phenomena connected with the change in the rate of setting of cements and studied the effects of salts like $CaCl_2$, $Ca\,(NO_3)_2$, $(NH_4)_2\,CO_3$, etc. He arrived at the conclusion that salts producing insoluble compounds with $Ca\,(OH)_2$ accelerate setting, while those forming soluble salts retard it. The same subject was studied by Dr. Rohland[2] last year. He ascribes the change in the rate of setting:

1. To the disintegration of the coarser cement particles to finer ones.

2. Change in the condition of the aluminates.

3. Excessive amount of alumina.

4. Formation or introduction of one or more catalytic agents.

He makes a list of catalytic agents, positive or negative, accelerating or retarding the hydration, including—

Calcium sulphate	—
Aluminium chloride	+
Sodium carbonate	+
Calcium chloride	+
Barium chloride	+
Potassium bi-chromate	—
Calcium chromate	—
Sodium chloride	0

The relation between the already existing velocity of reaction and the effect of a plus or minus catalytic agent is expressed by the statement:

1Thonindustrie Ztg., 1902, No. 66.
2Thonindustrie Ztg., 1902, No. 49.

Where the velocity of reaction (setting) is very slow, the catalytic agent produces a greater effect than in those in which the velocity is greater. Positive and negative reagents may neutralize each other. The quantities may be very small, one per cent. or less is often sufficient to produce great changes.

Dr. Bernhard Kosmann in 1902 discusses the constitution of Portland cement, and says that—"the imaginary tri-calcium silicate must be a basic meta-silicate in which two molecules of CaO are present, so that they are split off by the combination of water."

The study of the effects of sea water on Portland cement has occupied the attention of many European authorities owing to the great importance of the subject. The opinions in this respect are very much divided; some defend the Portland, claiming that good cement amply resists the dissolving action of the sea water, like Schuljatschenko, of Petersburg, while others like Chatelier, Rebuffat and Michaelis, seek to determine the weak points of the cement or to find a suitable remedy.

Thus Michaelis advocates the use of puzzolanic material, like trass, to be ground together with the cement. Chatelier claims that the starting point of the solution of the cement is the formation of calcium aluminium sulphate. This assumes dangerous proportions only if the content of alumina rises to four per cent., hence the alumina should be replaced by iron oxide. The dangerous quality of the alumina is decreased by an increase in lime and completely eliminated by silicious puzzolanes.

Rebuffat ascribes the action of sea water to sulfo-aluminates and says that the process is but a slight and superficial one, which does not harm the cement work to any appreciable extent.

In the United States, activity along the line of cement research was quite pronounced in the past year.

W. B. Newberry[1] examined the progress of burning in the rotary kiln by cooling a kiln sixty foot long, without emptying it. A constant reaction was observed from 840°C,

1 Cement and Engineering News 1902.

being shown by the change in color, and a constantly decreasing amount of volatile matter. Fourteen samples were taken at equal intervals. The most lively evolution of CO_2 took place between intervals 8–12(1030°–1425° C). The raw cement mixture at three was of a blue gray color, which between three and four becomes buff, retaining this color up to eight, when it changes to brown; at nine the lumps become harder; at eleven, they are vitrified on the outside, at twelve partially vitrified; at thirteen black.

Dr. Clifford Richardson (1902) has prepared synthetically non-dusting di-calcium silicates, as well as 3 CaO SiO_2 both hardening in moist air and water.

Prof. E. D. Campbell, of the University of Michigan, has carried on for several years, elaborate tests of cement mixtures, burning them in an experimental rotary kiln accompanied by accurate temperature measurement.[1]

"The minimum temperature required to burn Portland cement giving a sound cement with fresh clinker is 1450° C, for minimum contents of CaO. The temperature increases with the lime till in ordinary cements, it reaches 1550° C. The substitution of Al_2O_3 and Fe_2O_3 for SiO_2 lowers the overburning temperature, but may raise the temperature required for perfect boiling test. With a mixture low in CaO, the burning temperature for perfect boiling test is lowered by this substitution, but with mixtures high in calcium oxide the burning temperature required for the perfect test is raised and may become coincident with the overburning temperature. Any attempt to raise the overburning temperature by increasing the lime will fail to give a perfect hot test, even at the overburning temperature. The practical experience that lean clays (higher in silica) are safer than rich clays is verified. The effect of 8 – 9 per cent. MgO has but little effect on the temperature for perfect boiling test or over-burning temperature."

Professor S. B. Newberry assisted by Mr. M. M. Smith, also published a most valuable series of experiments.[2]

1 Journal American Chem. Society No. 10, 1902.
2 Cement and Engineering News, Nov. 1902.

He again reports having prepared 3 CaO SiO_2 by mixing the finely ground materials dry, and heating the mixture to a white heat. It does not, however, harden readily. No direct chemical proof of the 3 CaO SiO_2 is given. By fusing the mixture over the oxy-hydrogen blow pipe, the 3 CaO SiO_2 was found to be double-refracting, with rectangular cleavage, spec. gravity 3.022, is constant in volume, hardens well. A mixture of calcium carbonate and silica, heated for two hours at a red heat, leaves some SiO_2 uncombined unless at least $2\frac{1}{2}$ molecules of CaO to one of SiO_2 are present. At a white heat, the mono-, di- and tri-silicate mixtures become completely combined. The amount of water which a given cement will take up chemically, is a function of the mechanical conditions, porosity, etc. It may be as low as 10, or as high as 27 per cent.

On suspending finely divided calcium silicate in sufficient water to dissolve all the lime present, the residues are somewhat indefinite in composition, and continue to lose lime on prolonged action; they have, however, the following composition:

Tri-silicate (not fused), after twenty-nine and ninety-three days, 3 CaO 2 SiO_2 3 H_2O.

Tri-silicate (fused), 35 and 228 days, 2 CaO SiO_2 H_2O.

The di-silicate (quenched and dusted), did not change in composition, and did not hydrate.

The action of an amount of water insufficient to dissolve all of the lime present (100 cc's to 5 g) on the fused tri-silicate, for thirty days, followed by a treatment with sugar solution for 29 and 186 days, gives a residue approximately, 3 CaO 2 SiO_2 3 H_2O and 3 CaO 2 SiO_2 6 H_2O.

The work done for the Ohio Geological Survey in 1902 by the writer, though not completed, may be indicated by the following outline. It will form the substance of a special bulletin of the survey in the near future.

In the presence of clay substance, evolution of carbon di-oxide from amorphous calcium carbonate commences slightly at about 650° C, a drop in the rate of evolution is reached at 800° but resumed at 850°. At 1000° C the evolu-

tion of carbon di-oxide is completed. The lime begins to react with clay substance soon after the evolution of carbonic acid begins, the clay being completely decomposed at about 850° C. Free quartz begins to be attacked at about 950° C. Free silica coarser than the size between 120-150 mesh sieve is inert, at least at temperatures up to 1350° C. Feldspathic minerals are decomposed almost as readily as clay substance. Crystalline calcium carbonate is much more sluggish in reaction than the amorphous variety, especially at temperatures below 1100° C.

The chemical activity of calcium oxide was studied by grinding calcium carbonate intimately together with flint in a wet ball mill, so that a mixture of the formula 0.25 CaO SiO_2 was produced. This was burnt at 800°, 900°, 1000°, 1100°, 1200° and 1350° C, measured by means of the Chatelier pyrometer, these temperatures having been maintained for ninety minutes. After burning, the mixture was analyzed for each temperature, the total silica, the silica soluble in hydrochloric acid and sodium carbonate, the alumina and iron, and the carbon di-oxide being determined. The ground flint was examined in regard to its fineness of grain and was found to possess the following composition:

Left on 120 mesh sieve - - -	1.40%
Left on 150 mesh sieve - - -	2.36%
Left on 200 mesh sieve - - -	1.06%
Grains .0088 to .0004 inch diam. - -	24.74%
Grains .0016 to .0004 inch diam. - -	17.84%
Grains .001 to .0001 inch diam. - - -	9.30%
Dust below these sizes - - - -	43.30%

From the amount of soluble silicic acid and the amount of calcium oxide, the formula of the compound resulting from the action of the lime on the silica was calculated. It was assumed that owing to the large excess of silica, and to the intimate blending, the calcium oxide would show its maximum chemical effect under the above conditions of fineness of grain. These formula of course do not represent the act-

ual formula produced, since the exact amount of lime entering into reaction must remain an unknown quantity.

TABLE NO. I.

Temp. °C.	Per Cent. Soluble Silica	Per Cent. Available CaO	Sum of Soluble Silica Plus Available CaO	Carbon Di-Oxide Per Cent.	Formula
800	5.94	8.94	14.88	6.60	$CaO\ 0.7\ SiO_2$
900	6.44	16.40	22.84	1.30	$CaO\ 0.36\ SiO_2$
1000	3.62(?)	18.04	21.66	.....	$CaO\ 0.19\ SiO_2$
1100	17.11	18.04	35.15	.....	$CaO\ 0.887\ SiO_2$
1200	22.10	18.04	40.14	.....	$CaO\ 1.14\ SiO_2$
1350	22.73	18.04	40.77	.....	$CaO\ 1.18\ SiO_2$

This table seems pretty consistent with the exception of the 1000° determination, which is now being repeated. At 800°, apparently all of the free calcium-oxide has combined with silica, while at 900° there is evidently some lime uncombined, so that the formula appears distorted. It is evident the lime has united with no less silica than at 800°, but more calcium oxide is available than at the latter temperature. This is indicated also by the caustic property of this mixture. The best index of the activity of the lime is the amout of silica rendered soluble, especially if for 800° and 900° the carbon di-oxide is eliminated by calculation which will make the soluble silica 6.36 and 6.52 per cent. respectively.

Intimately associated with the progress of the chemical reaction between the calcium oxide and the silica, is the evolution of heat connected with it, at least for temperatures below 1300°C, when the lime is rendered inert as far as the measurable heat reaction is concerned. The heat produced must be ascribed mainly to the hydration of the calcium-oxide since it has been found by the writer that lime silicates evolve but little heat as will be shown by the following table of heats of hydration, determined on commercial cements. The values are expressed in calories per gram of cement, an excess of water having been used, 100 c.c. for from 3 to 5 grams. The cements, except when stated otherwise, were purchased in the open market and represent standard American brands, with the exception of one.

TABLE II.

HEATS OF HYDRATION.

No.	Kind of Cement	Calories Per Gram	Remarks
1	Portland Cement	1.786	
2	" "	1.190	European Cement.
3	" "	0.470	
4	" "	2.000	
5	" "	....	
6	" "	0.500	Obtained from manufacturer.
7	" "	2.100	
8	" "	2.200	
9	" "	5.560	Did not stand up well in boiling test.
10	" "	5.160	Did not stand boiling test.
11	Natural Cement	4.100	
12	" "	3.770	
	Natural (Magnesian) cement rock burned in large laboratory furnace for 1½ hours at		
13	400° C	No heat.	
14	500°	0.950	
15	600°	1.430	
16	700°	0.830	
17	800°	0.800	
18	1000°	0.470	
19	1100°	1.580	

The use of the calorimeter has been found of great value in judging a cement in regard to its fitness for use. I invariably use it for examining cements, before testing them. Owing to the cheapness of a good serviceable instrument and the comparative rapidity of a determination, this method of testing should find application by manufacturers.

Heat determinations were also made of various calcium and magnesium silicates which are given in the following tables:

TABLE III.

Composition	Temperature	Calories Per Gram	Composition	Temperature	Calories Per Gram
0.25 $CaO\ SiO_2$	700	1.60	2 $CaO\ SiO_2$	800	50.00
"	800	1.98	"	900	30.37
"	900	1.60	"	1000	2.50
0.5 $CaO\ SiO_2$	1100	0.88	"	1100	1 20
"	1170	0.50	"	1170	0.79
1.0 $CaO\ SiO_2$	600	.....	2.5 $CaO\ SiO_2$	600	2.96
"	700	2.98	"	700	7.54
"	800	1.70	"	900	29.37
"	900	7.34	"	1000	73.46
"	1000	19.85	"	1100	14.20
"	1170	0.80	"	1170	6.80
1.5 $CaO\ SiO_2$	600	0.70	2.8 $CaO\ SiO_2$	700	1.40
"	700	10.71	"	1100	72.85
"	800	15.08	"	1170	53.67
"	900	67.88	3 $CaO\ SiO_2$	700	0.91
"	1000	57.56	"	1100	27.96
"	1100	2.76	3.1 $CaO\ SiO_2$	1000	33.70
"	1170	1.19	"	1200	3.63
2. $CaO\ SiO_2$	600	.....			
"	700	1.59			

These mixtures were prepared from flint whose mechanical composition has been given and whiting containing 1.66% MgO, ground together for 8 hours in a wet ball mill. The heat evolved by the whiting alone was found to be 220.0 calories at 900°C, 195.5 at 1200. This decrease is due to the fact that some silica was absorbed by the whiting from the crucible.

Mixtures of whiting and 20 per cent. of kaolin were made, in order to study the effect of the clay substance upon the decomposition of the calcium carbonate, and the following hydration values were obtained:

TABLE IV.

Temp. ° C	Calories per gram.	Temp. ° C	Calories per gram.
700°C	.....	900°	126.43
800°	32.13	1000°	128.52

Similarly to the calcium compounds, magnesium silicates were prepared and tested in the same manner. These mix-

tures consisted of commercial magnesium carbonate and flint, finely ground together.

TABLE V.

Composition	Temperature	Calories Per Gram	Composition	Temperature	Calories Per Gram
0.5 MgO SiO_2	500°C	16.33	1 MgO SiO_2	800°C	5.55
do	600	10.10	do	900	.....
do	700	2.64	do	1000	1.58
do	800	1.78	do	1100	1.78
do	900	1.68	1.5 MgO SiO_2	500	20.15
do	1000	0.99	do	600	24.51
do	1100	0.90	do	700	12.30
1 MgO SiO_2	500	18.20	do	800	4.36
do	600	28.19	2 MgO SiO_2	500	17.27
do	700	5.71	do	600	.....

The magnesium silicates slake with extreme slowness and hence claim to satisfactory exactness cannot be made for the calorimetric determinations. The calorimetric hydration values of both the lime and magnesium series cannot be used as the basis of exact calculations of chemical composition; they can indicate only certain general tendencies, and hence are useful to this extent. In order to afford exact proofs, the determinations must be carried on much more extensively, and most laborious precautions must be taken in order to reduce errors to the minimum. In general, it may be said that the more basic the mixtures are, the greater is the error of the determinations arranged in the above tables.

The claim is being made by some that American Portland cements are not made as carefully as European cements, being insufficiently mixed and ground before burning. Though this hardly needs contradiction, the Ohio survey has examined a number of standard American cements in regard to the insoluble residue left after treatment with hydrochloric acid, sodium carbonate solution, and ignition, with the following results:

1. 0.14 per cent.
2. 0.47 per cent.
3. 0.46 per cent.
4. 0.51 per cent.
5. 0.59 per cent.

The most important factor in the manufacture of Portland cement is fine grinding of the raw mixture previous to

burning. In order to determine the actual fineness of raw cement mixtures, a number of samples were collected by visiting plants in operation, and making physical analysis by the Whitney suspension method. The following table will show the results of this work:

TABLE VI.

No.	Materials Used.	Grinding Machines Used	Residue on 80 mesh sieve. Per cent..	Residue on 120 mesh Per cent.	Residue on 200 mesh Per cent.	Grains .0088 to .0004 in. diam. Per cent	Grains .0016 to .0002 in. diam. Per cent	Grains .0011 to .00014 in. diam. Per cent	Finer than last size Per cent	Remarks.
1	Ferriferous limestone and shale	Emery mills for fine grinding	2.00	9.89	4.85	16.93	8.96	8.70	48.68	Ground dry.
2	Cement rock and limestone	Griffin mill	16.38	11.57	4.75	16.21	13.29	7.61	30.17	Ground dry.
3	Cement rock and limestone	Ball and tube mill	3.03	7.42	3.68	23.77	17.52	10.26	34.33	Ground dry.
4	Limestone and clay	Ball and tube mill (wet)	7.40	9.56	2.48	17.72	8.96	8.83	45.05	
5	Marl and clay	Wet tube mill	3.04	5.50	5.21	20.31	12.63	9.61	44.72	
6	Marl and clay	Wet tube mill	30.46	4.28	2.17	6.73	10.61	9.31	47.06	
7	Marl and clay	Wet tube mill	2.48	5.23	2.47	16.14	14.22	12.01	47.46	Shells in marl quite evident
8	Marl and clay	Wet tube mill	26.74	6.99	2.13	10.52	9.77	7.67	36.18	

The last column affords an index for judging the degree of fineness of the cement mixture.

The Whitney method of physical analysis can easily be modified so as to become useful in every laboratory. It may be carried out as follows: Take 5 grams of dried raw cement mixture, make up into a thin paste with water and wash through the 80, 120 and 200 mesh sieve respectively. Dry and weigh the residue on each sieve. The portion washed through the 200 mesh sieve is transferred to a 250 c.c. beaker and enough water added if necessary to make 200c.c. of slurry. Stir for one minute, let settle for one minute and syphon off carefully the supernatent liquid. Repeat this operation until the liquid is clear. Remove, dry and weigh the residue. The washings which have been removed are now boiled down to 200 c.c., stirred as before, allowed to settle for 3 minutes and syphoned off. This is continued till finally after 3 minutes the supernatent liquid is clear. The

residue is dried and weighed as before. The third washings are collected, stirred, allowed to settle for nine minutes, syphoned and washed as before. The sediment is dried and weighed. There are now found by sedimentation: First, a sediment, coming in size between the 200 mesh sieve and one minute's settling, which was found to range between 0.0088 inch and 0.0004 inch for quartz; second, a deposit from three minutes settling, ranging between 0.0016 and 0.0002 inch; third, a sediment, nine minutes settling, corresponding to a size of from 0.0011 to 0.00014 inch. The same method has been applied to burnt and ground Portland cement, though in this case, alcohol redistilled over caustic lime was used. The following table shows the size of grain of a number of commercial Portland cements:

TABLE VII.

No.	Grinding machine used.	Residue on 80 mesh sieve. Per cent.	Residue on 120 mesh sieve. Per cent.	Residue on 200 mesh sieve. Per cent.	Grains 0.008 to 0.002 in. diam. Per cent.	Grains 0.002 to 0.0002 in diam. Per cent.	Grains 0.0007 to 0.0003 in. diam. Per cent.	Grains below last size. Per cent.	Removed by screens Per cent.	Tensile strength 1 cement; 3 sand lbs. per square inch in 28 days.
1	Tube mill.....	7.07	14.56	4.45	22.68	19.29	7.36	24.69	25.98	.....
2	Tube mill.....	9.01	15.35	5.09	21.50	20.53	7.06	21.52	29.45	318
3	Tube mill.....	12.12	15.05	7.61	21.11	16.85	5.91	21.37	34.78	303
4	Tube mill.....	14.11	14.57	7.82	22.43	13.95	7.81	19.32	36.49	.....
5	Tube mill.....	3.84	17.64	5.10	25.27	17.56	10.16	20.42	26.58	297
6	Griffin mill.....	3.06	15.41	8.24	28.56	16.48	12.74	15.51	26.72	350
7	Griffin mill.....	9.43	16.91	6.37	25.52	12.18	9.20	18.49	32.71	313
8	Griffin mill.....	5.00	15.42	14.52	27.30	19.10	9.22	14.88	29.53	285
9	Griffin mill.....	4.40	11.35	5.13	23.79	21.30	10 01	24.01	20.89	346
10	Griffin mill.....	4.18	13.30	5.07	22.63	14.64	12.31	28.79	22.55	314
11	German cement..	3.88	15.84	7.63	27.63	17.83	13.30	13.89	27.36	281
	Natural cements.									1 cement: 1 sand
12	Mill-stones.....	7.36	9.93	3.53	16.42	13.98	14.74	34.04	20.82	317
13	Tube mill.....	10.53	12.85	8.50	11.39	22.15	20.72	13.85	31.89	299
14	Mill-stones.....	12.50	11.59	4.29	16.52	21.95	17.42	15.76	28.37	265

It is evident that these data are not sufficient to disparage any particular machine, as the mode of operation,

the rate of feeding, etc., govern to a large extent the fineness of the output. The figures given do show however, how fine commercial cements are being ground. The tensile strength of the various cements, of course, is not solely a function of the fineness, but is dependent much more on the proper chemical composition, thorough blending of the raw mixture, good burning and the length of storing.

Besides these tests, the writer has about completed a large synthetic series of cement mixtures, burnt at different temperatures, intended to show the function of the chemical composition in regard to producing hydraulicity.

The first series is to show the hydraulic strength of synthentical cements, of the Roman cement type, burnt at 900°, 1000° and 1100°C. As the basis of the cement composition, there were used the formulae: $X(2.5\ CaO\ SiO_2) + Y\ (CaO\ Al_2O_3)$; $X\ (2.0\ CaO\ SiO_2) + Y\ (CaO\ Al_2O_3)$; $X\ (1.5\ CaO\ SiO_2) + Y\ (CaO\ Al_2O_3)$; $X\ (CaO\ SiO_2) + (CaO\ Al_2O_3)$.

The clayey material was introduced two-fold; first, by kaolin, 46.4 per cent. SiO_2, 39.7 per cent. Al_2O_3, 13.9 per cent. H_2O; second, by a mixture of kaolin and flint, containing 70 per cent. SiO_2, 22.21 per cent. Al_2O_3, 7.7 per cent. H_2O. The silica-alumina ratio in the first case is 1.17 : 1, while in the second, the ratio is 1 : 1.69. The lime was brought in as whiting of the best quality, which of course, is the same as ground limestone.

The mixtures were ground wet in a porcelain ball mill for six hours and heated for two hours at the tempertures given. The results of this series of tests are shown in Table VIII on the succeeding page.

The American natural cements and the presence of so much dolomite in Ohio, suggested the replacement of the CaO molecule by the double molecule $MgCO_3\ CaCO_3$ in equivalent proportion. The experiments were carried out as those of table VIII. A natural Ohio dolomitic limestone was used. The results of this series are given in Table IX.

TABLE VIII.

No.	Clay Base.	Formula of Cement.	Temperature.	Tensile strength 1 cement: 1 sand. 28 days. lbs. per square inch.	Remarks.
1	Kaolin	2.5 $CaO\ SiO_2$ / $CaO\ Al_2O_3$	900C	.....	Briquets broke Softened.
2	do	do	1000	.....	
3	do	do	1100	.....	Not tested.
4	56% kaolin 44% flint	do	900	181	
5	do	do	1000	225	
6	do	do	1100	.....	Not tested.
7	Kaolin	2.0 $CaO\ SiO_2$ / $CaO\ Al_2O_3$	900	20	Softened.
8	do	do	1000	183	
9	do	do	1100	.....	Not tested.
10	56% kaolin 44% flint	do	900	182	
11	do	do	1000	218	
12	do	do	1100	111	Set too rapidly
13	Kaolin	1.5 $CaO\ SiO_2$ / $CaO\ Al_2O_3$	900	37	
14	do	do	1000	108	
15	do	do	1100	46	Softened.
16	56% kaolin 44% flint	do	900	216	
17	do	do	1000	211	
18	do	do	1100	208	
19	Kaolin	1 $CaO\ SiO_2$ / $CaO\ Al_2O_3$	900	.....	Softened and broke.
20	do	do	1000	96	
21	do	do	1100	71	
22	56% kaolin 44% flint	do	900	188	
23	do	do	1000	166	
24	do	do	1100	46	

A great many interesting features are brought out by the last two tables, which I lack space to discuss. In general, table VIII indicates that the temperatures 900, 1000, 1100°C are too low to bring out the full hydraulicity of the mixtures. The kaolin seems less efficient than the kaolin-flint mixture.

Table IX shows that we are dealing with a narrow temperature range of hydraulic activity. Whether the breaking down of the silicates is due to the two rates of hydration, the slow one of magnesia and the rapid one of lime cannot be said definitely, but seems probable. Here also the kaolin-flint mixture is more effective than the pure kaolin.

TABLE IX.

No.	Clay Base.	Formula of Cement.	Temperature.	Tensile strength 1 cement: 1 sand; 28 days. lbs per square inch.	Remarks.
25	Kaolin	$2.5(CaMg)OSiO_2$ $(CaMg)OAl_2O_3$	850°C	261	
26	do	do	950	320	
27	do	do	1050	148	
28	56% kaolin 44% flint	do	850	175	
29	do	do	950	235	
30	do	do	1050	284	
31	Kaolin	$2.0(CaMg)OSiO_2$ $(CaMg)OAl_2O_3$	850	82	
32	do	do	950	80	
33	do	do	1050	.....	Soft, broke.
34	56% kaolin 44% flint	do	850	251	Works up well.
35	do	do	950	256	
36	do	do	1050	48	
37	Kaolin	$1.5(CaMg)OSiO_2$ $(CaMg)OAl_2O_3$	850	.....	Broke.
38	do	do	950	.....	Briquets broke.
39	do	do	1050	.....	
40	56% kaolin 44% flint	do	850	89	
41	do	do	950	324	
42	do	do	1050	.....	Briquets broken
43	Kaolin	$1(CaMg)OSiO_2$ $(CaMg)OAl_2O_3$	850	.....	Briquets br'ke in clip.
44	do	do	950	.....	do
45	do	do	1050	.....	
46	56% kaolin 44% flint	do	850	337	
47	do	do	950	313	
48	do	do	1050	.....	Briquets broke in handling.

The survey has extended this series to a higher temperature and has also embraced the Portland cements in a similar set of experiments.

The Portland cement series seems to show that high silica clays invariably produce the best cements, provided of course, that the mixture contain the proper lime ratio, is ground sufficiently and burnt thoroughly. The addition of free silica as sandstone is in many cases of great benefit. In order to do this economically, the stone should first be calcined in a vertical or any other suitable kiln and quenched with water while hot. It should be ground separately, being

added to the mixture in a ground condition. This is due to the fact that quartz does not grind well when enveloped by particles of clay.

The addition of a small amount of iron ore often assists vitrification and improves the behavior of poor cements.

It appears that rotary kiln clinker contains the greater part of its iron as ferric-oxide in spite of the black color of the clinker.

Our knowledge of cements must be built up step by step, synthetically and analytically, by a natural reasoning process and cannot be increased by purely hypothetical assumptions. Too much theorizing and not sufficient experimental work has been done.

NOTE BY SECRETARY: This paper was read by title at the Boston meeting and consequently received no discussion. Discussion is now specially invited, and if submitted in writing will appear in future volumes of the transactions.

NOTE ON VAPOR GLAZING.

By Lawrence E. Barringer, E. M. in Cer.,
Schenectady, N. Y.

In a paper on "The Relation Between the Constitution of a Clay and its Ability to take a Good Salt Glaze," which appeared in Vol. IV of the Transactions of this Society, the writer showed the exact relation between the glaze and body of the Logan ware, as well as other facts connected with the process of salt-glazing, and the points brought out may be applied to salt-glazed wares in general. It is the object of the present note to criticise certain statements made by Mr. Wilton P. Rix* in a paper entitled "Note on the Vaporous Method of Glazing Pottery" which to the writer appear far from accurate in the light of his own work along this line.

Mr. Rix ascribes the decline of vaporous glazing to the demand for cheapness and for uniformity of texture and color. This is probably true with reference to salt-glazing fine wares and the process is no doubt in decadence in this country in the stoneware industry. But for coarse wares such as bricks, sewer-pipes, conduits, etc., these very points of cheapness and uniformity put the salt-glaze in a class of its own. For these products there is certainly no cheaper method and the practice is well established and flourishing for this class of clay goods.

After mentioning three distinct processes of vapor glazing, namely, (a) the development of a carbonaceous atmosphere in the kiln, to have a reducing effect, as in lustres, (b) the development of a plumbiferous atmosphere as in smeared wares and (c) the development of alkaline atmosphere as in salt-glazes; and remarking that only the two latter involve the essential principle of vapor glazing, Mr. Rix goes on to discuss salt-glazing and says concerning the temperature employed, "Neither does the action of glazing take place

*Trans. No. Staff. Cer. Soc., 1, 1901-02, 26-33

except at a temperature of about 1200°C." This sounds final and is certainly to be taken as meaning that good success in the work is not attendant upon temperatures lower or higher than that mentioned. In the salt-glazing kilns of Logan, however, the temperature is regularly 1350°C or more,—never less. And in certain sewer pipe works which have come to the writer's notice, the glazing heat is about 1140°C. In the first place a fire-clay is used for the body, and in the second place a shale. Certainly it seems that Mr. Rix should either modify his statement or else specify the nature of the body to which this is applicable.

As to the chemical composition of the body, Mr. Rix recommends *highly* silicious clays for, he says, "The chemical action of the salt upon the ware only takes place upon the silicious particles of the ware." To this I wish to make vigorous objection. An analysis of the Logan salt glaze gives the following composition:

$$\left.\begin{matrix} 1.326\ Na_2O \\ .003\ K_2O \\ .297\ CaO \\ .003\ MgO \end{matrix}\right\} \left\{\begin{matrix} 1.000\ Al_2O_3 \\ .078\ Fe_2O_3 \end{matrix}\right\} \left\{ 4.418\ SiO_2 \right.$$

Where do the other ingredients apart from soda and silica, particularly alumina, come from, if not from the body? It was also shown by the experiments carried out by the writer that silica alone could not be salt-glazed, and that a clay base was as necessary to the operation as free silica. In fact, a combination of clay base and free silica is necessary in the body to be salt-glazed, and the proportions of these must be such that the ratio of alumina to silica will fall within the limits of

1.00 alumina :4.6 silica
1.00 " :12.5 "

As a rule all the constituents of the body are attacked by the salt fumes and there results a soda-alumina-silicate with small proportions of alkaline earths and iron included in the glass.

Alluding to the sand particles in the body, Mr. Rix asserts that the best results are obtained when these particles are very fine, that is, able to pass through a 120 to 140 mesh sieve. Referring again to my experiments along this line I

would call attention to the conclusions arrived after trials of sands of different finenesses (from 40 mesh to floated flint which would not settle in water in twenty minutes) namely, "As regards brightness, smoothness of finish of the salt glaze, it makes but little difference whether the free silica in the clay is fine or coarse," and I have great confidence in the accuracy of the work performed which led to this conclusion. Fineness of sands affects color, but not texture.

Concerning the kiln atmosphere Mr. Rix says, "If the salt is introduced into a reducing atmosphere, the color of the ware must inevitably be dark and blackish in appearance, nor can this result be remedied afterwards." The writer has taken a brick on which was a salt glaze, light green in color, and again placed it in a kiln and the second time it came forth a dark brown. The same brick put into a kiln the third time came out a light green again. Furthermore, the brick in the bag walls of salt-glazing kilns are light in color after some firings, and dark after others. The color of the salt glaze is subject to change, therefore, but whether this can be controlled throughout an entire kiln has not yet been demonstrated.

With reference to cooling the kiln during salting this statement appears in Mr. Rix's paper, "In dealing with salt glazing, the process of the introduction of the salt necessarily involves the loss of heat through the inflow of cold air through the aperatures by which the salt is introduced, and it is possible by this means so far to lower the temperature of the kiln that the surface of the ware is no longer in a condition to favor a chemical action, the salt being merely deposited on the surface. For this reason, it is generally desirable to add the total amount of the salt in two or three portions, increasing the temperature by a light firing between each addition." As to the dissociation of the salt being an endothermic reaction, by which the kiln is very considerably cooled, Mr. Rix says nothing whatever. Why should opening the fire doors to introduce salt cool the kiln more than would be the case in the introduction of coal at each firing? In salting, the temperature of the kiln is unquestionably lowered, but I think there can be no doubt

but that most of the cooling is due to the heat-consuming reaction which takes place during salting and that the kiln can not be said to be seriously cooled by the mere opening of aperatures to introduce salt. In some plants, it is the custom to mix with the salt resin and crude oil, or other substances high in calorific value, to prevent chilling of the kiln during salting by the rapid combustion of these substances. Mr. Ira A. Williams* has shown how the amount of resin and oil required to theoretically supply the heat units consumed by the dissociation of each unit of salt may be calculated by a study of the reactions involved. It would seem that Mr. Rix has overlooked the main cause of cooling during salting.

While the points brought out in my previous paper were based on careful experimental work, covering several months and are reliable statements, I am sure, I do not hold that they are all indisputable by any means. But differing conclusions should come from careful tests and observations and in Mr. Rix's paper no reference is made to any preliminary work upon which he based his statements. In reading the paper, one can only accept most of the assertions as being the personal opinions of the author.

The subject of salt-glazing offers a wide field for experiment, and one that presents much that is indeed interesting.

DISCUSSION.

Mr. Alfred Yates: Do I understand from this paper, that salt glazing is wholly unreliable as to color, and is liable to be dark or bright, or whatever it happens to be? The color is entirely due to the burner. If the burner will properly prepare his fires, rake up and clear them, so he has a perfectly oxidizing flame, and put the salt on it in that state, he will get a bright color every time. That is my experience.

Mr. Karl Langenbeck: Mr. Wilton Rix says that if what you give as the necessary preliminary steps are not taken, then the color cannot be brightened afterwards by an oxidizing fire. And it seems to be the claim of Mr. Barringer that taking a brick that is greenish and not bright, he has put it

*Brick, Vol. XIV, No. V.

into an oxidizing fire and changed the color, which Mr. Rix asserted flatly would not be the case.

Professor Edward Orton, Jr.: Mr. Barringer did not say anything about reliability of color. He said that Mr. Rix had made a statement, which his own experience did not bear out, and that he had found that a salt glaze *could* be reduced and oxidized back and forth.

Mr. Langenbeck: Perhaps Mr. Rix had this practical point in mind; if a fire has been crowded, and the kiln is possibly spoiled so far as the appearance of the ware is concerned, the color of the kiln as a whole cannot be recovered in good condition. Mr. Barringer's statement would be no answer to that fact. Probably Mr. Yates has had some experience in recovering a kiln of ware which had been spoiled by the burner, and has that in mind in making his statement?

Mr. Yates: I know if you have a carbonaceous flame, you will have a spoiled kiln. The fires must be perfectly clear, and if they are, you will get a reliable uniform color.

Professor H. A. Wheeler: Yes, if you salt once or twice, and then rake up and work your fires and get them into proper condition, the second salting will be all right; but don't salt unless the fire is all right.

Professor Orton: Doubtless these recommendations sound very satisfactory, but I do not think they wholly settle the case. I know of one plant where they use natural gas, and maintain probably as nearly perfect oxidizing conditions as can be obtained in any kiln, and yet their results do not follow out the course indicated by Mr. Yates. In this same plant, I have repeatedly seen bricks with green ferrous colorations, mixed with yellow or brown ferric colorations, and yet the firing was said to be done under oxidizing conditions. I mention this as showing that there are a good many unsolved problems in connection with the matter.

I have from that factory a piece of salt glazed ware made in the shape of a funnel, the coloration of which is brown on one side, and green on the other. What is more, the brown covers one half exactly, and the green covers the other half exactly, the line between being as sharply defined as you

could draw with a piece of chalk. I happened to get possession of the piece by asking the manager of the plant how he accounted for these occasional green bricks mixed among the brown ones. He said he did not know. I said, "You always find them in the same relative places, don't you? That is, you find the green ones where they were out of the current of the gases during the cooling of the kiln, and the brown ones where they were well exposed." He said, "Oh no; you are mistaken. You are liable to find the green bricks right in the middle of a wall of brown ones, where the same gases must have bathed the surface of each alike." I expressed incredulity, and said I would like to see an instance, but he said he had no kiln open at that time, but he was perfectly satisfied that he was right.

Up to this point, you can see I was very much inclined to view these green and brown colorations as being purely oxydation and reduction phenomena, as Mr. Yates and Prof. Wheeler seem to think. But, as I still remained unconvinced, the manager brought out this funnel, one half of one color and one half the other. I immediately said that the piece had been pressed in two halves, and that the clay or treatment had not been the same before burning. This he denied, stating that the two halves were made by the same man from clay from the same pile which had been tempered and brought up to him in one quantity and put in a box to keep it from drying out too fast.

If this were all true, I was compelled to admit that bricks might show an equal divergence in color under the same treatment in the cooling or salt glazing. But it seems to me impossible to account for this change of color on the re-oxidation theory.

It seems to me necessary to assume some difference in the treatment of the two halves of that funnel. I don't believe it could be a matter of oxidation and reduction, when it was sitting on the top of the other wares, exposed to the same gases, both in setting and cooling. I cannot see how the gases could strike it in such a way as to make so sharp a line of divison between the two colors. It must be a difference either in the clay body, or in the treatment of the

two halves. A difference in the clay body might easily have occurred, but the manager was emphatic in saying that no such thing did occur. He said one half was pressed just before noon, and the other half immediately after the man came back from dinner.

It might be said that one half was lying longer in the mold, and took up more saline matter from the mold than the other. But Mr. Barringer in his work on this subject made some experiments on this point by adding small additions of calcium sulphate and magnesium sulphate to the same clay. The effect was to make the trial pieces take on an unusually rich brown salt glaze, even where a very small quantity had been added. It was a very much darker, handsomer glaze than when the clay was glazed without the addition of these soluble sulphates. It does not appear from the test that either half of this particular funnel bore any relation to the presence of these salts from the mold. In fact, the color phenomena in this plant are most remarkable, and I think I have said enough to show that it cannot be explained by any superficial recommendations like merely salting when the fires are clear.

Mr. Yates: I want to ask a question about this place. They burned natural gas, you say. Do they burn with a blue flame or not?

Professor Orton: No, sir, the flame in the firebox is white or incandescent. It might be blue, at lower temperatures.

Mr. Yates: If it gets too blue a flame, it becomes almost incandescent. If the kiln is worked by a damper, that creates currents. The minute the burner dampers his kiln, he loses combustion, and instead of a blue flame, he gets a carbonaceous flame, and where that flame strikes, it produces a difference in color.

Mr. Langenbeck: I would like to bear out Mr. Yates' observations, and still claim that something further must be brought to bear, than that the mere method of passing in the gaseous fuel creates uniformity in color. The mixture of gases in a kiln is much like a mixture of liquids in a vessel. Anyone who has played with a mixture of colored

liquids in water, has noticed how long a time the eddies of colored liquid will pass through the water in all directions before making a uniformly colored liquid.

Anyone who have observed with any degree of interest, the red porcelains originally made by the Chinese and Japanese, with a slight addition of copper to their glaze, which under certain conditions is a pale tint, and again a brilliant one, will have noticed this. Their white porcelain body has been glazed by dipping into a uniform glaze in the slush tub, so the glaze must be the same throughout the entire body, but you will find almost invariably that the brilliant red on the reduced oxide of copper is on certain prominent places, looking as though a flame had struck the body and skirted off the depressions. I don't know whether I make myself understood. (Going to a blackboard) We have, for instance, a little vase or tea jar with a section like this, (illustrating) of Seger porcelain. That will be flamed red all around here, (indicating) and up to this lip, and there, and around this turned-up edge of the foot. I could imagine it caused by the swirls of oxidizing flame like (illustrating), and swirls of reducing flame right beside them, causing a softening all around it. We have to keep before us the mixtures of gases in the kiln, which even if it is a gaseous one is still full of swirls and inequalities.

Mr. Stanley G. Burt: Mr. Chairman, two points have occurred to me in connection with this question of a red color being developed on one side of a piece and not on the other. The finest ox-blood red I ever saw, was in a piece gotten by Mrs. Bellamy Storer. She made a piece of ware one morning and put it in the kiln and turned on the gas and then went away and forgot about it. It was well after lunch time when she recollected it, and rushed down to turn off the gas, expecting to find the piece ruined. When she took the piece out of the little kiln, she found the side of the sagger had cracked, and through this crack the gas had played on the ware, striking the piece on one cheek, as Mr. Langenbeck has explained. There is this gorgeous spot of red where this crack was, all the rest of the piece being in the natural green of the higher cupric oxide.

Another point in the paper which to me was very interesting has not been called up, and I would like to hear it discussed. Mr. Barringer makes the statement that the question of fineness of grain of the silica hasn't anything to do with the formation of the salt glaze, but it does affect the color. I think we have not heard from those discussing this paper about this question, and I would like to have it explained. It is a very interesting point.

Professor Orton: In Mr. Barringer's tests, fine silica produced a remarkable lightening in color. Take the clay Mr. Barringer experimented on, and add to it, say, two parts of coarse silica and the color of the ware is little changed. But add the same quantity of fine floated silica, and the color of the salt-glazed piece is very much lighter. The change in color may come in two ways. The same silica being fine, is distributed in many hundred times more grains and thus affects the color of the body, rather than the glaze. And secondly, the sodium may take up fine silica so much more easily than it does coarse silica, that it preys less on the ferrugineous body materials, and makes a lighter, clearer colored glaze. Perhaps both reasons enter into the explanation.

Mr. Isaac Hardy: What little experience I have had along that line bears out what is in the paper. The finer the clay, the lighter the goods; the coarser the clay, the darker the goods. I have never thought much about the matter, but I should think that with the finer clay you would have the denser body; with a coarser clay, a more open body, and the sodium vapors can get more iron out of the clay, and this makes a darker colored glaze.

Mr. Frank W. Walker: Before the discussion on this paper closes, I would like to say that this is the kind of paper that this Society should encourage. The criticism of previous papers, the drawing out of points of difference in the views of different members are of the greatest importance. In that way we will get the real value of the papers which have been presented at previous meetings, much better than from the discussion which takes place at the time the paper is read. I believe this is the first thing we have

had in the way of criticism of a previous paper, and I hope that the example will be imitated hereafter.

Professor Wheeler: The question as to the influence of the fineness of the silica seems capable of very simple explanation. In the case of sewer pipe, if your clay is coarse, you get a very thin film of glass covering and hiding the oxide of iron. The free oxide of iron gives color to the material, and if the flame happens to be oxidizing it will be dark; if reducing, light. If, however, the silica is in a very fine state of division, you will produce such a large amount of glass, and of such high fluxing value, that all the iron will pass into some chemical condition which is not a silicate of iron; in that event, its coloring influence is very slight. You will recall that there are some minerals of very high percentage of iron, but not of strong color, because the iron is in a combined condition. Other minerals, however, with a low percentage of iron, in free state, will have more powerful colors. I think in the one case, the iron is fixed; in the other, partially. I rather think that is the probable solution.

UNDERGLAZE CERAMIC COLORS.

By Edward C. Stover, Trenton, N. J.

To attempt anything like an exhaustive set of experiments in systematic order on Ceramic Colors generally, and the various ways in which they are applied, and to show how each would be affected by the various fluxes and hardening substances used with them, and how affected by glazes, of all the different compositions, and of the varying quantities of each of the constituents, and at the various heats in general use, and also on the different kinds of bodies, would involve trials running way up into the thousands, to say nothing of the stained slips, and stained glazes, as well as other glaze or enamel colors.

Seger has correctly stated that the Ceramic Colors can only be determined by trial. This statement can readily be verified by making some trials to prove any theories that may be set forth regarding colors.

My first scheme of the trials to be made for this paper was based on the use of seven oxides, viz.: Cobalt, Copper, Nickel, Manganese, Chromium, Uranium and Iron, and also a prepared Chrome-Tin pink, making eight different color trials to run. I also expected to use two reducing mixtures; first, a flux taken from J. E. Corfeld's recipe book; and second, a spinel of each color according to the Seger formula. All of these combinations were to be tried on three different bodies, viz.: bone-china; vitreous, hotel china; and white granite. Further, each color was to be tried in four ways—1st print underglaze, 2nd print on the glaze, 3d ground-laid on glaze, and ground-laid under glaze. These were all to be fired in a glost kiln, under seven types of glazes, and were to be fired at six different heats, Cone 02, 3, 6, 8, 10 and 12. But as this line of experiments would involve over 8000 trials, and would necessitate my having the greater portion of them fired by some of my friends, to

get the desired heats, it was absolutely essential that the series of trials should be materially reduced. Finally, the trials as presented here, numbering 1152, were made along the following lines:

The seven oxides above referred to, including the tin-pink, were treated with the Corfeld flux, and as spinels, under nine different glazes, fired at cone 6, and nine glazes, fired at cone 8, on two kinds of bodies, bone-china and vitreous tile, in two ways each, underglaze and on glaze, all fired in glost kilns.

Each trial has been marked in underglaze black on the back, by the cone number, serial number of glaze, by the letter indicating the oxide, and with a dash under the oxide letter indicating underglaze; those without this dash were put on, on the glaze, and all fired in glost kiln. The trials marked with a small $\underline{s}$ were spinel, while those without this letter were half oxide and half Corfeld flux.

The spinel mixtures were made, and calcined in biscuit oven, covered, but to allow air. They were compounded according to the Seger method of spinel as follows:

NiO	0.5	MgO	0.5	Al_2O_3	1.0
CuO	0.5	"	0.5	"	1.0
MnO_2	0.5	"	0.5	"	1.0
Cr_2O_3	0.5	"	1.0	"	0.5
Co_3O_4	0.5	"	1.0	"	0.5
Fe_2O_3	0.5	"	1.0	"	0.5
U_3O_4	0.5	"	1.0	"	0.5
2 CaSn CrO_3	0.5	"	1.0	"	0.5

The Corfeld flux has the following chemical composition:

$$\left.\begin{array}{l} K_2O\ 0.72 \\ PbO\ 0.07 \\ CaO\ 0.20 \end{array}\right\} SiO_2,\ 3.33$$

made as follows:

Flint,	500
Pearl Ash,	100
White Lead,	50
Whiting,	50
Nitre,	50

calcined in glost oven, covered, but to allow air.

Both the Corfeld flux, and the spinel, were very finely ground on glass slabs before being applied.

The nine Cone 6 glazes were all mixed raw from the following formulae:

No. 1—	K_2O 0.3 CaO 0.6 ZnO 0.1	Al_2O_3 0.22,	SiO_2 2.00
No. 2—	PbO 0.3 CaO 0.6 ZnO 0.1	Al_2O_3 0.22,	SiO_2 2.00
No. 3—	Na_2O 0.3 CaO 0.6 ZnO 0.1	Al_2O_4 0.22,	SiO_2 2.00
No. 4—	BaO 0.3 CaO 0.6 ZnO 0.1	Al_2O_3 0.22,	SiO_2 2.00
No. 5—	ZnO 0.3 CaO 0.6 SnO 0.1	Al_2O_3 0.22,	SiO_2 1.00 Sb_2O_3 1.00
No. 6—	Na_2O 0.3 CaO 0.6 ZnO 0.1	Al_2O_3 0.22,	SiO_2 1.40 B_2O_3 0.60
No. 7—	MgO 0.3 CaO 0.6 ZnO 0.1	Al_2O_3 0.22,	SiO_2 2.00
No. 8—	K_2O 0.3 CaO 0.7	Al_2O_3 0.50,	SiO_2 4.00 B_2O_3 1.00
No. 9—	K_2O 0.19 CaO 0.48 ZnO 0.13 PbO 0.20	Al_2O_3 0.26,	SiO_2 2.68 B_2O_3 0.30

The nine Cone 8 glazes were mixed raw according to the following formulae:

No. 1—	K_2O 0.3 CaO 0.6 ZnO 0.1	Al_2O_3 0.26,	SiO_2 2.90
No. 2—	PbO 0.3 CaO 0.6 ZnO 0.1	Al_2O_3 0.26,	SiO_2 2.90
No. 3—	Na_2O 0.3 CaO 0.6 ZnO 0.1	Al_2O_3 0.26,	SiO_2 2.90
No. 4—	BaO 0.3 CaO 0.6 ZnO 0.1	Al_2O_3 0.26,	SiO_2 2.90
No. 5—	ZnO 0.3 CaO 0.6 SnO 0.1	Al_2O_3 0.26,	SiO_2 2.80 Sb_2O_3 0.10
No. 6—	Na_2O 0.3 CaO 0.6 ZnO 0.1	Al_2O_3 0.26,	SiO_2 2.30 B_2O_3 0.60
No. 7—	MgO 0.3 CaO 0.6 ZnO 0.1	Al_2O_3 0.26,	SiO_2 2.90

$$\text{No. 8—} \quad \left.\begin{matrix} K_2O & 0.3 \\ CaO & 0.7 \end{matrix}\right\} \; Al_2O_3 \; 0.50, \quad \left\{\begin{matrix} SiO_2 & 4.00 \\ B_2O_3 & 1.00 \end{matrix}\right.$$

$$\text{No. 9—} \quad \left.\begin{matrix} K_2O & 0.19 \\ CaO & 0.48 \\ ZnO & 0.13 \\ PbO & 0.20 \end{matrix}\right\} \; Al_2O_3 \; 0.26, \quad \left\{\begin{matrix} SiO_2 & 2.68 \\ B_2O_3 & 0.30 \end{matrix}\right.$$

It will be noted that numbers 8 and 9 are the same in both series, number 8 being the glaze made from Cone 4 formula with one equivalent of boracic acid added, as produced by Dr. Hecht, of Berlin; and number 9 of both series being the glaze commonly known as the Trenton glaze. Both series were fired at Cone 6 and Cone 8, including the last two glazes without change, as above stated.

It will be noticed from the trials[1] that the No. 1 glazes, both Cone 6 and Cone 8, finished slightly dull, and that the colors are brighter with the Corfeld flux, than with the spinel.

The number 2 glazes, both Cone 6 and Cone 8, were fairly bright; colors brightest with the flux.

The number 3 glazes, both Cone 6 and Cone 8, were fairly bright; colors brightest with the flux

Number 4 glazes, both Cone 6 and Cone 8, were slightly dull; colors brightest with the flux.

Number 5 glazes, both Cone 6 and Cone 8, were dull and wrinkled; none of the colors were well developed.

Number 6 glazes, both Cone 6 and Cone 8, were dull or mat, and crazed on the vitreous tile; the colors were not well developed, especially the pink.

Number 7 glazes, both Cone 6 and Cone 8, were dull and wrinkled with the spinel, and a mat finish with the flux, pink particularly bad.

Number 8 glazes, both Cone 6 and Cone 8, were bright; colors all bright with the flux, except uranium; colors all bad with the spinel, except uranium.

Number 9 glazes, both Cone 6 and Cone 8, were bright; colors all bright with the flux, except pink; all bad with spinel.

1 The 1156 trials mentioned were mounted in rows and exposed during the session for the inspection of the society.

It will be noticed that very little difference, if any, exists in any of these trials between placing the color under the glaze, and placing it on the glaze, when fired in glost kilns.

It will be seen by the trials, that the differences in colors are more marked between the Corfeld flux and the spinel, than the differences produced by the different glazes, which would seem to justify the conclusion that the proper way to control the color and hue, would be by adopting the correct flux or hardening substance, and to regulate the tints and shades by the proportions of oxides and the mixture adopted.

By comparing the result of this series of trials, with the series of copper-green, stained-glaze trials, presented by Mr. Walker at our Cleveland meeting last year, it seems that the oxides, when reduced by fluxes or hardening substances, and used as underglaze colors, will produce a greater uniformity of color, than they do when they are actually calcined into fritt, which forms a part of stained or colored glazes.

Judging from the two series, it would seem necessary in underglaze work, to get, and permanently fix, the variety of colors, in the varying tints and shades of each, by calcining the oxides with the proper substances to produce the desired hue and tone. This would make a very interesting series of trials, and we are in need of data along this line.

It was with the hope of partially filling this gap, that the trials here presented were made, and this paper undertaken, and I must confess, that the results are far from being what I had originally hoped, and expected them to be. While plenty of underglaze colors are to be had, and numerous recipes for making same, yet all who are interested must certainly feel the want of any systematic record, along the lines above suggested.

If the effort made should be the means of stimulating further trials and research along this line, which should ultimately give us a means of permanently fixing any desired color in its varying tints and tones under good workable glazes, I will feel repaid for the effort.

DISCUSSION.

Mr. F. W. Walker: The amount of work which the members of this society are willing to take upon themselves in preparing papers for these meetings is astonishing. This paper of Mr. Stover's is an illustration of the point. Mr. Stover has made over eleven hundred trials, of which he presents about half of them here; so you can see what amount of work he has done. This is also another illustration of the great difficulty of discussing papers without opportunity for studying them in advance.

Dr. Edward Hart: I think what Mr. Stover needs more than anthing else, is some help. I would suggest in that line, as he has had difficulty in burning spinels, that he seek help from the electrical art. I undertook some work in the ceramic line myself, in the making of silica tubes. This was described to us at the Niagara meeting of the Electrical-Chemical Society last September. Since that time, Mr. H. H. Potter, of the Sawyer-Mann Electric Company, of New York, has been working along the same line, and not more than a month or two ago, I was in his laboratory, and found he had silica tubes there. A peculiar and interesting property of silica is the co-efficient of expansion, which is almost nil. You can heat them up, and plunge into water, and they will not crack. It struck me that I might make silica vessels, for boiling down chemicals. You can do almost anything in chemistry, if you only have something to do it with. The trouble is that some of these chemicals attack everything you put them in. I have already succeeded, I may say, in making a vessel about four inches in diameter of silica fused by the electric arc, and I would say to Mr. Stover that he can fuse his spinels by electric arc. The principal difficulty which I find is to keep the carbon out of the mixture. I presume there would be difficulty in getting these sesqui oxides fused without turning them into proto-oxides.

Mr. Karl Langenbeck: I would like to ask Mr. Stover whether any colors were applied faintly, so as to have an opportunity of judging of the relative solubility in the glaze of both spinel colors, and those made with Corfeld flux.

Mr. Stover: All were put on with a thin coat, then a thicker coat, then a couple of lines, to see what effect the thickness would have. In this one (indicating), fired at Cone eight, it stood very well in all thicknesses. In the majority of cases the colors fluxed with the Corfeld flux were best. I really consider the whole spinel series a failure, for the reason that they were not brought to a perfect degree of fusion.

Mr. Langenbeck: It has been a long time since I read the note of Seger in which he speaks of the making of underglaze colors on the spinel basis. My recollection is that his point was, that a color which approximates the character of a spinel, resists better the solvent action of the glaze. I do not think that preparing the color alone as a spinel is sufficient to make a complete underglaze of it. My impression is that the spinel should be formed as the chromo-genic body, which should be suitably fluxed. I think the trend of future work on this subject should be, not a comparison of the spinel body directly with an oxide flux, but a comparison of a spinel chromo-genic body suitably fluxed, with an agent to make it adhere to the glaze and develop its color, in comparison with a straight oxide flux.

THE NEW DEPARTMENT OF CLAY-WORKING AND CERAMICS AT RUTGERS COLLEGE.

By Cullen W. Parmelee, B. Sc., New Brunswick, N. J.

The establishment of this department is not Rutgers' introduction to usefulness in the field of ceramic industry. We interested in the old institution have a great deal of pride in the many notable services rendered the state by the late Dr. George H. Cook, a vice-president of the college. Conspicuous among his good works is the report on the New Jersey clays which he investigated as State Geologist, assisted by Dr. J. C. Smock, also of Rutgers. The report of 1878, needs no eulogy for the admirable manner in which the subject was treated.

Then should have followed the organization of a school of ceramics. It was not until the year 1901, however, that an effort was made to secure legislation toward this end. It was defeated, but the gentlemen interested believed thoroughly in the project, and were not to be discouraged. By diligence and generalship the recalcitrant legislators were brought into line and in 1902 passed the bill with but one dissenting vote. By the act $12,000 was appropriated for equipment and $2,500 for maintenance during the year 1903. Money for succeeding years must be annually voted.

In accordance with the terms of the law, the school performs the two-fold function of providing for instruction and for investigations, the director being charged with the duty of publishing in a convenient and accessible form the results of his researches.

The fiscal year of the state terminates on October 31st, and the balance of any appropriation unexpended at that time reverts to the state. You can readily understand that the four months in which I had to undertake and to complete the equipment and the organization were busy months, but very happily, I had the experience of Professor Orton and Professor Binns to draw upon. Permit me, to express my appreciation of their interest and helpfulness.

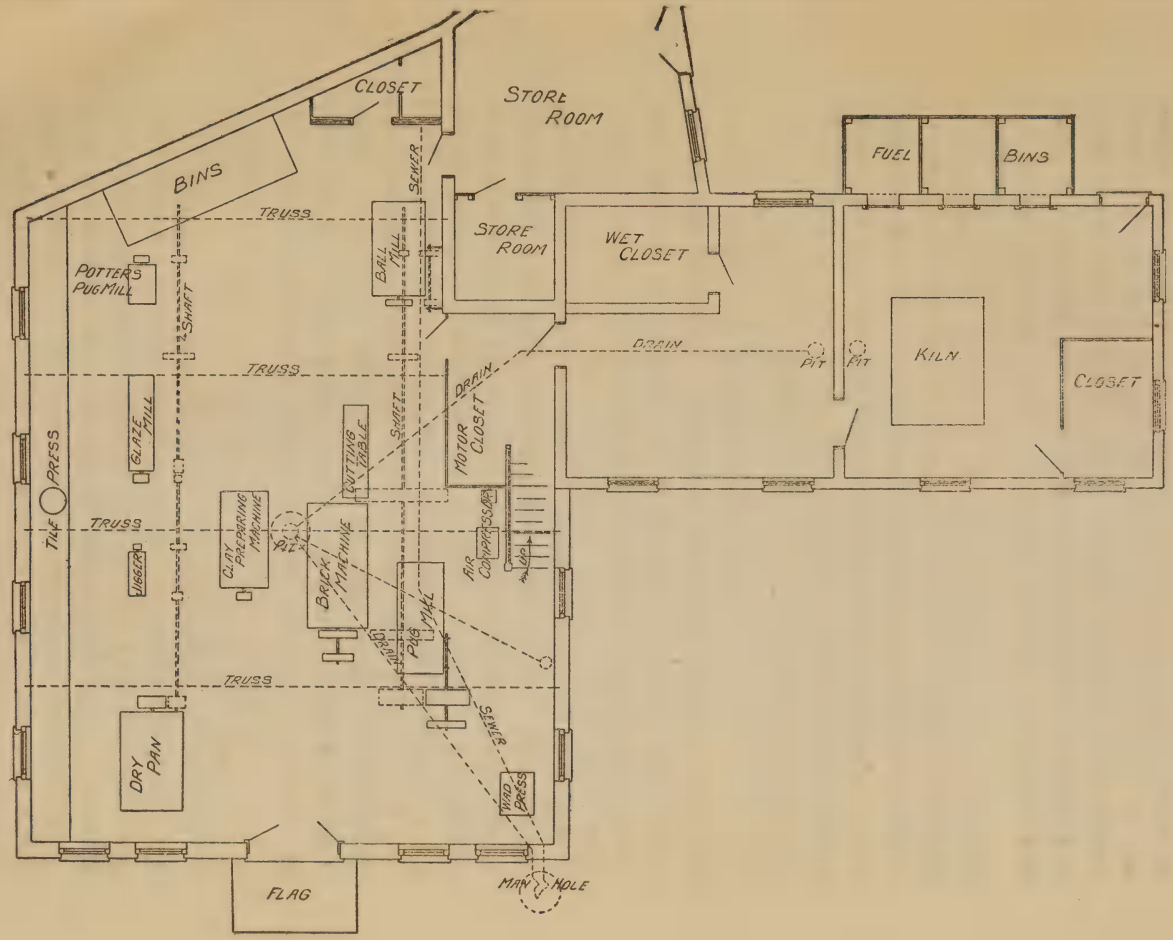
PLATE 1. EXTERIOR VIEW OF THE MAIN WING.

Our first need was proper accommodations. There was no suitable place in any of the college buildings, and with one small appropriation we could not afford to erect a fine large new structure. There was one college property however, a two-story brick building, unused, but which formerly served in the humble capacity of a barn. This had six small rooms, in all a floor space of about 1600 square feet. We accepted this as neuclus and added thereto an equivalent number of square feet in the form of a one-story brick addition.

This new portion serves for our machinery room. It has a good cement floor, pitching slightly toward the center, where there is a grating and pit with sewer connections. On one side of this room stretches a work bench forty feet long. Numerous windows furnish good light; ample gas and water supply is provided, also toilet facilities. Connected with this room is the store room which conveniently opens on a court with alley connection to the street. Another adjoining room contains one wet closet which serves in lieu of a cellar. This is an inclosure 6x9 with cement floor, soft brick walls and terra cotta lumber ceiling and an iron door. The interior can readily be made wet by a hose, and when closed will retain its dampness for a long period. The interior is lined with racks for shelving.

Next is the kiln room. This is at the end of the old building and separated by a brick partition wall. It is only 20x27, and of course our fuel bins had to go outside, ports being cut through the wall to give access to the fuel. One kiln has been built and there is room for another small one. In its place temporarily rests a wooden closet 6x9, provided with shelves and designed for the storing of ware for drying preparatory to firing.

In the second floor of the old portion, two rooms are used, one for a library, museum and class room. Its walls are lined with cases having sliding glazed doors. This affords space for the display of our ceramic collection, that is, for the smaller pieces. In the workshop, a shelf has been built on three sides of the room at about eight feet above the floor, this is intended for the large coarser wares. In the small room


CLOSET
STORE ROOM
FUEL
BINS
BINS
SEWER
TRUSS
BALL MILL
STORE ROOM
WET CLOSET
POTTERS PUGMILL
SHAFT
TRUSS
DRAIN
PIT
PIT
KILN
CLOSET
GLAZE MILL
SHAFT
CUTTING TABLE
MOTOR CLOSET
TILE PRESS
TRUSS
CLAY PREPARING MACHINE
PIT
BRICK MACHINE
AIR COMPRESSOR
VINEGAR
PUG MILL
TRUSS
DRY PAN
SHAFTS
WIND BRESS
FLAG
MAN HOLE

we have provided shelving for our literature on ceramic topics, a considerable collection being already gathered.

The director's office and his laboratory is also on the second floor. As the ceilings were low and under a flat tin roof, it was decided to light and ventilate this room by means of an eight foot square iron and glass skylight with two movable transoms on each side. The floor is one inch asphaltum laid on the old flooring. This has the advantage of being waterproof and practically fireproof. There is the usual equipment of working table, sink, hood and wall case for supplies.

Metal ceilings have been used where ceilings had to be provided. They are clean, attractive in appearance, and may readily be kept so. Cement has been used for flooring on the ground floors excepting in the kiln rooms, which is clay.

The gas supply is brought into the building by an $1\frac{1}{2}$ inch pipe, and none of the piping is less than $\frac{3}{4}$ inch. This is of course a generous provision for such a small building, but it insures an adequate supply.

In securing the equipment I found the manufacturers of machinery very kindly disposed toward the project. In every case the machinery was purchased at special prices, and in many instances at figures which made them practically gifts.

Power for running our machinery is furnished by a 30-horse power, 4-pole 250 volt motor furnished by the General Electric Company. This power is transmitted by two lines of shafting, each 33 feet long, with self-oiling adjustable hangers, and carrying, with two exceptions split steel pulleys.

The machinery consists of brick machine outfit, potter's and tile maker's appliances. Its arrangement can be seen on the plan. The brick-making machinery consists of three pieces, all furnished by the American Clay-Working Machinery Company. They are an auger brick machine of a capacity of 20,000 brick per day, a five-foot horizontal pug mill and a side-board delivery cutting table. All these are large pieces, requiring much power, a considerable quantity of raw material and are really too big for an experimental

plant, but are the smallest practicable machine obtainable.

The potter's outfit was furnished by the Crossly Manufacturing Company, of Trenton, N. J. It consists of:

A four-foot grogmill with blank plates which may be used when run as a wet-pan. The mullers have a five inch face.

A variable speed jigger and pull down and throwing wheel combined. On this, pieces as large as a ten inch jardiniere may be made.

A four-jar glaze mill, the jars having a capacity of about two gallons each. They are made of a porcelain body and furnished with flint pebbles.

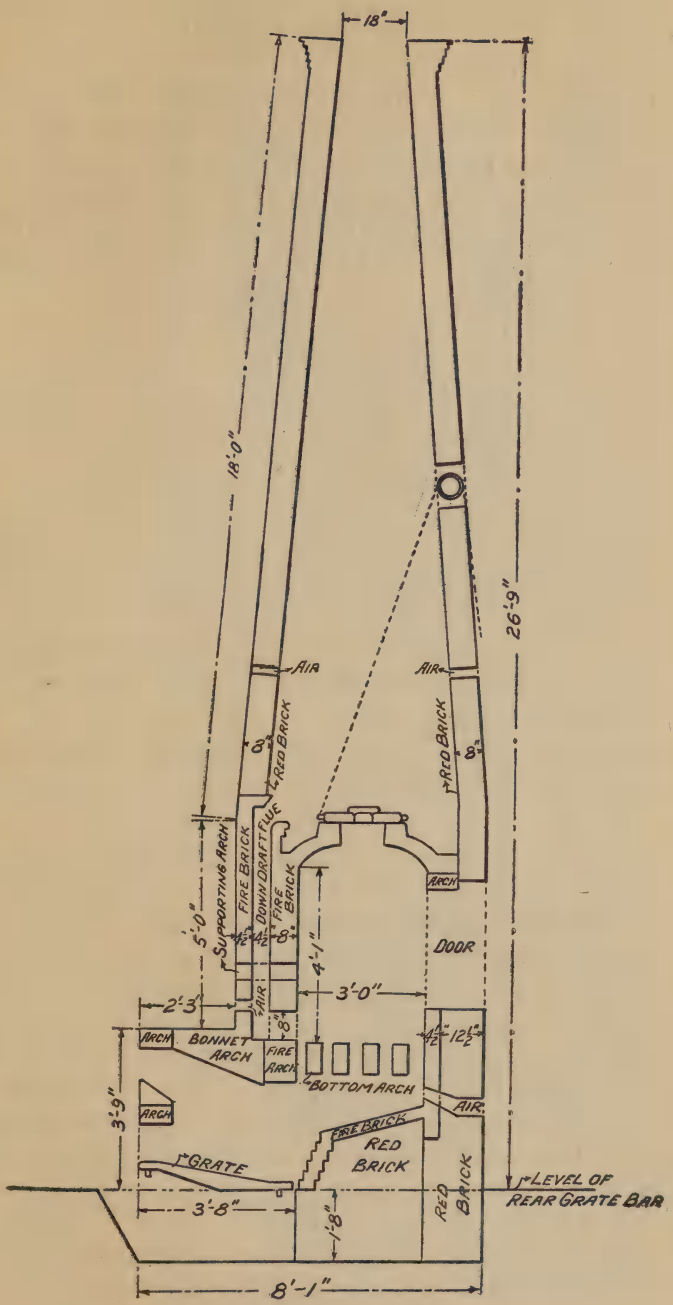
A twelve-inch potter's pug mill.

A clay preparing machine which is an attractive and compact arrangement of blunger, agitator, lawn screen, slip pump and filter press. It has a capacity of from 500 to 1,000 pounds a day. There are 20 plates in the filter press, each 9 inches square, and the press can be filled in about thirty-five minutes.

There are also a small tile press, a hand jigger, a mould maker's jigger, a wad mill and a stilt press. For grinding large quantities of material we have a large ball mill with a one piece lining 2 inches thick. It has internal dimensions 3 feet by 2 feet.

For use with a Deville furnace, we have a Crowell rotary pressure blower which is capable of furnishing pressure of ten pounds to the square inch.

We have provided only one kiln, as our present needs and resources limit our expenditures. It is designed however, to do the work of both the up-draught and down-draught, which is provided for in this wise: The kiln space is three feet square by four feet high; the floor is made by the tops of four arches which spring from the sides at the level of the grate bars. When used as an up-draught, the flames and the gases arising from the fire-box, pass upward through the spaces between the arches, up through the kiln space and into the stack, through openings in the crown. For down-draught purposes, these openings in the crown are closed. Quarries of the same length but lacking four inches


18"
18'-0"
26'-9"
AIR
AIR
8"
RED BRICK
8"
RED BRICK
SUPPORTING ARCH
FIRE BRICK
DOWN DRAFT FLUE
FIRE BRICK
4½"
4½"
8"
5'-0"
4'-1"
ARCH
DOOR
2'-3"
AIR
3'-0"
8"
ARCH
BONNET ARCH
FIRE ARCH
BOTTOM ARCH
4½"
12½"
3'-9"
ARCH
AIR
FIRE BRICK
RED BRICK
GRATE
LEVEL OF REAR GRATE BAR
3'-8"
1'-8"
RED BRICK
8'-1"

of the width, are laid on the floor of the kiln space. Quarries are placed vertically near the side wall and two inches therefrom, leaning against projecting bricks. To prevent the falling backward of these, provision has been made for the insertion of bricks to support these vertical quarries parallel to the side walls. Having done this, we have provided flues against the side walls. The flames and hot gases rising through these are deflected by the crown and drawn into a flue opening in the end wall of the kiln near the floor. This flue empties into the stack above the crown.

The fire mouth is designed for soft coal. The grate-bars have an area of 880 square inches. They are three feet eight inches long, and have a drop of about five inches.

The damper is a fire-clay disc hooped and hinged to a ring about the crown. It is controlled by means of a chain which runs through a pulley in the side of the stack and this opens and closes the one foot circular opening in the crown.

The kiln is eight feet one inch long, five feet eleven inches wide. From floor to top of hob is three feet nine inches; from top of hob to shoulder is five feet; from shoulder to top of stack is eighteen feet.

Unfortunately I cannot give any results of firing owing to the fact that we have not had opportunity to give it a thorough test.

We have also a Deville furnace, a gas furnace for fritting, and a Seger test kiln improved by Heincke. We are provided with an electric pyrometer and Seger cones.

Two courses of study have been arranged. One covering a period of four years, the other, a short course. In the former the student will have a liberal training in the related sciences with especial emphasis placed upon general and analytical chemistry. During the latter two years he specializes on ceramics. General and economic geology, raw materials, bodies, glazes, drying and firing are topics studied in the lecture room, and experimented upon in the laboratory.

The short course is offered for the practical man who has had experience in clay-working and who recognizes the

PLATE 2.—DIRECTOR'S OFFICE.

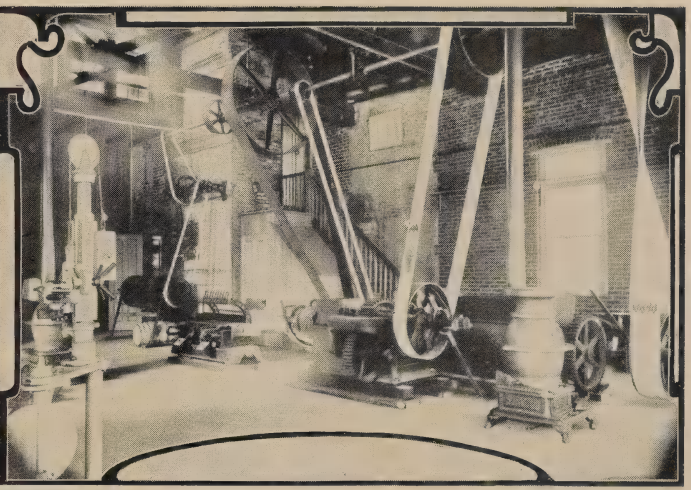


PLATE 3.—MACHINE ROOM.

value of scientific training, but is unable to undertake the full course.

We have at present seven students, and the indications for the future are bright.

DISCUSSION.

The Chair: I am sorry Mr. Bloomfield could not have been here, to have heard Professor Parmelee's paper. We really owe a great deal to our friend Bloomfield, for he certainly worked hard and persistently for three years, to the end that New Jersey should have a ceramic school. His work with the legislature was invaluable, and he really is the father of the school.

Professor Orton: This society undoubtedly recollects the part it had in the establishment of this plant for teaching ceramics. We lent our influence, whether it was great or small, toward pushing the bill through the New Jersey legislature last winter. For myself, I am much gratified to see the description of other ceramic schools becoming a part of our records of progress. With a multiplication of facilities along this line such as is surely coming, we can't help producing a class of men which will aid materially in the work of our society and in the greater and larger end to which this society stands pledged, that of building up the ceramic industries of this country. There is certainly no state in which a ceramic school could more suitably be started than New Jersey, which stands well toward the top among the clay-working states of the Union. I think the society should welcome this addition to the list with all hail.

Mr. Langenbeck: I do not know that I can say anything in addition to what has been said, but I have been much interested in the movement, and felt very much gratified at the energy with which Professor Parmelee has taken hold of the work. Ordinarily, they do not feel quite certain yet as to the benefit of the application of science in the pottery industry, but I am happy to say that I have heard many cordial expressions of interest in this case from potters of Trenton.

THE INFLUENCE OF MAGNESIA ON CLAY.

By Adolph E. Hottinger, Chicago, Ill.

Under the above title, Dr. Mäckler read a paper before the German Society for Clay, Cement and Lime industries. Being very much interested in this paper, I made some experiments on the subject and give some results that I obtained, and also some of the original.

A brief summary of the paper in question shows that the action of magnesia on clays is a subject to which little attention has been paid; but, from the results obtained, it is shown that exceedingly valuable properties are given to clays carrying this element naturally or into which it is introduced.

The characteristics of clays of this nature are that they may be made into ware of extreme length and with very thin walls, which may be very nearly vitrified, and still be kept perfectly straight and true. Also, that where exact shapes are required, especially in vitreous ware, clays of this nature are valuable.

The reason of this is in the melting and vitrification point of clays of this nature. Lime and its influence on clays is well understood, and it is well known how near together the vitrifying and melting points lie. Clays carrying magnesia are very different in their behavior; and the melting and vitrifying points are farther apart, and such clays consequently can be made into vitreous ware, without great care in burning.

Another interesting fact developed is that kaolin with magnesia gives dense bodies at comparatively low temperatures, in distinction from lime, which has but little action at the same temperature.

Some trials made on this line show interesting results. Mixtures were made as follows, and the absorption taken of trials burned at cones one and five:

Number of Test.	Mixtures.	Absorption.	
		Cone 1.	Cone 5.
A 1.	Kaolin 100, Whiting 10	34.7	30.2
A 2.	Kaolin 100, Magnesite 10	25.2	17.1
A 3.	Kaolin, without additions	25.5	24.7

I also quote mixtures as made by Dr. Mäckler:

Number of Test.	Mixtures.	Absorption.	
		Cone 1.	Cone 5.
J.	Kaolin 100, Marble 25	24.8	23.9
K.	Kaolin 100, Marble 12½	24.7	24.1
L.	Kaolin 100, Magnesite 21	16.4	18.9
M.	Kaolin 100, Magnesite 10½	18.8	15.9
	Zettlitz Kaolin, with addition	25.9	18.3

From the last experiment it will be seen that Dr. Mäckler used the lime and magnesia in equivalent parts, and by observing the mixtures M and K, at Cone 5, having equal equivalents of lime and magnesia, the latter lowered the absorption of the trial M 8.2 per cent. over the trial K. It is also noticed that lime in J and K lowered the absorption over the original kaolin somewhat at Cone 1, while at Cone 5 the absorption is 5.6 per cent. greater than that of the kaolin.

I was not able to get results anywhere near the lime mixtures, as given, but approached closely to the magnesia experiments. This is probably due to a difference in mixing, and probably in material used. Dr. Mäckler's mixings were all made in a slip state, and were ground in a mill, while I made mine dry, first rubbing them together in a mortar and afterward sifting twice. This would not give as intimate a mixture as the original; but the result shows the advantage of the use of magnesia.

To get an idea of what advantage magnesia might be in a porcelain mixture, I made some trials with lime, magnesia and also dolomite, containing 50.28 per cent. calcium carbonate, and 40 per cent. magnesium carbonate, etc. The idea was to use dolomite as a source of magnesia.

For the porcelain body I used the formula of the Berlin porcelain as given by Seger:

Clay Substance,	55.
Feldspar, -	21.2
Quartz, - -	23.5

The mixtures are as follows:

Number of Test.	Mixture.	Absorption.	
		Cone 1.	Cone 5.
B 1	Porcelain Body 100, Whiting 10,.....	26.2	24.9
B 2	" " 100, " 5,.....	22.0	11.8
B 3	" " 100, Dolomite 10,.....	20.2	12.4
B 4	" " 100, " 5,.....	19.1	10.8
B 5	" " 100, Magnesite 10,.....	18.8	9.9
B 6	" " 100, " 5,.....	13.2	6.0
.....	Porcelain Body, without addition.....	22.5	14.4

B 6, of this series, at Cone 5, proved to be the best, being a very hard, close body, which cannot be scratched with a hard steel point. B 3 and 4, containing the dolomite, are an improvement over the whiting, but cannot equal the magnesia mixtures.

An interesting fact developed by the experiment is that, used in equivalent amounts, magnesia will not give the same result as lime.

As an instance of this, the Cone 4 mixture was taken, consisting of 0.3 equivalents Feldspar, 0.7 calcium-carbonate, 0.2 kaolin, 1.8 quartz. In this mixture, the lime was replaced by an equivalent of magnesia, and the mixture fired to Cone 1. A cone made from the lime mixture was vitrified, while the magnesia cone was still porous. Firing to Cone 5, the magnesia cone is vitrified, but still remained standing, and showed not the least sign of melting, the corners remaining perfectly sharp. Not having any higher cones in the kiln during this experiment, the fire was raised until Cone 4 was melted to a nearly clear glass, and when this point was reached the magnesia cone had gone down.

A series of experiments with a shale of the following analysis:

Silica,	62.66
Alumina,	21.26
Ferric Oxide,	3.50
Calcium Oxide,	0.92
Magnesium Oxide,	0.54
Alkalies,	4.60
Volatile and loss, on ignition,	6.44
	99.92

also showed some interesting results, in particular the difference in the melting points of the shale, with the lime and magnesia added.

The following mixtures were made as follows:

No. of Test.	Mixture.	Absorption.			
		Cone 05.	Cone 1.	Cone 3.	Cone 5.
C 1	Shale 100, Whiting 25,	21.9,	Melted,	Melted,	Melted,
C 2	Shale 100, Whiting 12½,	20.4,	Vitrified	Melted,	Melted,
C 3	Shale 100, Magnesite 21,	32.8,	7.3	Vitrified	Shape retained,
C 4	Shale 100, Magnesite 10½,	28.4,	0.32	Vitrified	Slightly swelled,
C 5	Shale 100, Dolomite 22,	22.4,	11.5	Parti'lly melted,	Melted,
C 6	Shale 100, Dolomite 11,	17.7,	12.1	Blister'd	Melted,
	Shale, without additions.	12.0,	0.78	Blister'd	

It is noted from the above that C 4 is practically vitrified at Cone 1, and does not show signs of distress until Cone 5, when it swelled slightly.

The dolomite mixture did not come up to expectations and showed less range in their melting and vitrification points than the lime mixtures, as at Cone 1 they are still very porous, while at Cone 3 they had started melting, and had lost shape.

DISCUSSION.

Mr. Hottinger: I did not intend this as a paper, but merely as a note on a line of experiments which I thought would be of interest.

Mr. E. C. Stover: I think Mr. Hottinger's paper is one which needs no apology. I am glad to see that he has

reached out a little into the field of our German friends, and has taken up a line of work suggested thereby, and brought the results here. We have enough here to work out ourselves, yet we cannot offord to ignore the work of the other world. If those who read the German technical papers do not do this work, the rest of us will lose much that we ought to know. This question of finding a material to operate as a flux in a vitreous body, which will widen the range between the point of actual vitrification and the point of viscosity, is a point we are all interested in. As shown by Mr. Hottinger, with whiting as a flux, these points lie close together, and a flux which will widen these points will be important to anyone working in vitrified bodies.

Mr. Hottinger: That is illustrated by taking this shale and adding the magnesite to it. At Cone 1, the cone with the whiting melted. Taking the same mixture with magnesite, it showed no signs of melting until Cone 5 was reached, and under the experiments shown in the Germon paper, not even at Cone 7 did it show signs of melting, though it swelled slightly, and it took a good deal beyond that to bring it to a glass. Another point shown by the German paper is that in porcelain or vitreous wares, where exact shapes are wanted—for instance, electric porcelain—magnesite plays an important part. You will note that in the porcelain mixture it did not show swelling. In the shale mixture, firtd above the vitrification point of the shale, there was slight swelling.

The Chair: In the porcelain mixture, does it show swelling at a certain point?

Mr. Hottinger: I did not try it for that. I tried to show what effect magnesite has upon the mixture at Cone 5.

The Chair: That touches right on the point I am going to bring up later as regards this swelling for electric insulators, (exhibiting samples). Many of the electrical porcelain pieces as now made are quite intricate, it being necessary for them to fit expensive metal parts, and they must necessarily be exact. I have brought with me two samples which show that point of swelling. Such pieces which are slightly blistered and swelled must be rejected, because they will not

fit the metal portion of the apparatus which they are made to complete.

Professor Edward Orton, Jr.: As I understand it, in the paper presented by Mr. Hottinger, one of the chief points of value is the demonstration of the fact that magnesite as a flux will enable us to get vitrification at actually lower temperatures. So it not only widens the range of vitrification, but enables us to use lower temperatures than otherwise.

FURTHER STUDIES ON WHITE BRISTOL GLAZES.

By Ross C. Purdy, Columbus, O.

In as much as formula I:

$$\left.\begin{matrix}0.5\ K_2O\\0.4\ ZnO\\0.1\ CaO\end{matrix}\right\}\ 0.55\ Al_2O_3\ \left\{\begin{matrix}3.30\ SiO_2\\.01\ Na_2B_4O_7\end{matrix}\right.$$

as developed in my article on "Stoneware Glazes" before this society last year, was a surprise to those familiar with the formulae of Bristol Glazes most generally used in the stoneware industries today, because of the relatively higher equivalent content of potash and alumina and low ratio existing between the alumina and silica, it is the object of this paper to prove or disprove the points in question.

From the following formulae which show the composition of the glazes actually in use among representative stoneware factories, it will be noted that the majority of them do not agree with the above formulae I in the use of such high equivalents of either potash or alumina.

TABLE I.

	K_2O	CaO	ZnO	Al_2O_3	SiO_2
II	0.237	0.327	0.433	0.347	2.275
III	0.225	0.388	0.386	0.356	3.450
IV	0.327	0.300	0.373	0.366	2.540
V	0.208	0.434	0.358	0.332	2.780
VI	0.403	0.201	0.395	0.473	2.960
VII	0.377	0.180	0.444	0.516	2.840
VIII	0.278	0.194	0.527	0.403	1.920
IX	0.342	0.305	0.322	0.418	2.220
X	0.199	0.461	0.340	0.306	2.630

It is not a surprise then to learn that the practical potters who use glazes of these compositions should look askance at such a radical change as advised in formulae I. The fact is, however, that the two giving the best satisfaction are VI and VII. They are the best in regards to opacity, gloss and general working qualities; thus indicating

that better results *can* be obtained by use of a higher equivalent of potash and alumina than *is* the general practice.

It must be admitted, however, that on a commercial basis, glaze No. I did not prove satisfactory. The fault, however, did not lie in the use of a too high content of alumina. It had a good gloss and was very opaque; so, from a chemical standpoint, it was correct. But its physical properties were such as to make it very unsatisfactory as a glaze. It crawled very badly. In fact, it drew up into large globules. It was impossible to handle the ware after it had been dipped because large patches of the glaze would scale off.

Further experiments were made with glaze I as a basis, to discover and remedy the trouble.

It is not necessary at this time to give all the experiments made, because the cause and solution of the trouble can be illustrated by giving only the formulae of the best glazes deduced.

TABLE II.

	K_2O	CaO	ZnO	Al_2O_3	SiO_2
XI	0.405	0.194	0.405	0.505	2.845
XII	0.450	0.150	0.400	0.600	3.250
XIII	0.370	0.230	0.400	0.500	2.900
XIV	0.375	0.225	0.400	0.500	3.125

These glazes were used on a commercial scale under similar conditions of firing and on the same clay, giving satisfaction in all respects.

Two facts are to be observed by comparing glazes XI, XII, XIII and XIV with I.

1st. That it is possible to use as high as 0.55 equivalents of alumina.

2nd. That it is not feasible or possible in the case in question, for physical reasons, as well as chemical, to use so high an equivalent of feldspar; which means, as a sequence the lowering of the equivalent of potash.

The formulae of several glazes which had crawled have been given* Their equivalents of alumina ranged from

*Vol. IV Trans. A. C. S., p. 66.

0.55 to 0.75. The deduction was drawn that the use of such high equivalents of alumina and consequently large equivalents of clay was the prime cause of the crawling. But in the light of the present experience, I now beg to modify that statement.

In all these glazes, except two which were thus cited, the feldspar content ranged from 0.50 to 0.55 equivalents, and in the two exceptions noted, the equivalent of ZnO was above 0.4, which in itself is a prolific source of crawling.

It is seen then, that glaze I crawled so badly because the per cent. of feldspar was too high, thus creating physical difficulties which could not be counterbalanced by the supposed increase in fusibility obtained from the use of the larger amount of feldspar. The physical limitations from the addition of large quantities of feldspar arising in a Bristol Glaze are as positive as the chemical limitations and of equal importance.

In the light of formulae XI, XII, XIII and XIV, it is seen that 0.5 equivalent of feldspar is not necessary for the proper maturity at Cone 7 of a Bristol glaze having 0.55 equivalent alumina, which is in contradiction to statements made by the writer last year.[1] In fact, the use of 0.40 feldspar make a more fusible mix than does 0.5 equivalent.

Clay workers generally consider that refractoriness is *always* in proportion to the alumina, but this is not true as will be shown.

Seger[2] made into cones the following mixtures, by compounding 1.0 equivalent of feldspar successively with 1.0, 2.0 and 3.0 equivalents of carbonate of calcium.

$$\text{No. 1—} \left.\begin{matrix} 0.50\ K_2O \\ 0.50\ CaO \end{matrix}\right\} 0.50\ Al_2O_3,\ 3.0\ SiO_2$$

$$\text{No. 2—} \left.\begin{matrix} 0.33\ K_2O \\ 0.66\ CaO \end{matrix}\right\} 0.33\ Al_2O_3,\ 2.0\ SiO_2$$

$$\text{No. 3—} \left.\begin{matrix} 0.25\ K_2O \\ 0.75\ CaO \end{matrix}\right\} 0.25\ Al_2O_3,\ 1.5\ SiO_2$$

He was surprised to find, notwithstanding the fact that the RO's were increased by decreasing the alumina and

1 Transactions of A. C. S., Vol. IV. Page 69.
2 Translation of the Collected Writings of Herman Seger, Vol. I, Page 232.

silica, that each of the mixtures were more refractory than the pure feldspar.

Mixtures of clay with feldspar, and flint with feldspar similarly increased its refractoriness. But he found that when calcium carbonate and clay together were added, the result was quite different.

From the tables of Seger's trials the following facts can be noted:[1]

1st. That each of the several mixtures of feldspar, quartz and marble adopted as a basis of his several series, were made more fusible by the addition of 0.5 equivalent of kaolin.

2nd. That his notes on the same experiments indicate that in all mixtures where the quartz content is not more than six equivalents, even 1.0 equivalent of kaolin made them but a trifle, if any, less fusible than when only 0.5 equivalent of kaolin was added.

3rd. That in series IV which has for its base

$$\left.\begin{matrix}0.25\ K_2O\\0.75\ CaO\end{matrix}\right\}\ 0.25\ Al_2O_3,\ 3.0\ SiO_2$$

the addition of 1.0 equivalent of kaolin actually makes it more fusible than where 0.5 equivalent of kaolin is added.

4th. That in the most fusible mixtures, the content of alumina ranged from 0.5 to 0.75 and never fell below 0.5.

5th. That "it appears distinctly that neither the glazes lowest in alumina are really the most fusible ones, nor those with a higher content of alkali, but that for low fusibility there must evidently be a *definite proportion between* the *alumina* and *fluxes*."

In the discussions under this same topic last year, formulae and samples were exhibited, illustrating this same fact of the increased fusibility incurred by the addition of 0.05 equivalent of clay to mixtures which contained no clay but which had 0.5 equivalent alumina.

Professor Wheeler[2] quotes Dana's table showing the fusibility of feldspars.

1 Translation of the Collected Writings of Herman Seger, Vol. I, Pages 234-236 inclusive.

2 Missouri Geological Survey. Vol. XI, Page 147.

TABLE III.

Name.	Silicate Degree.	SiO_2.	Al_2O_3.	K_2O.	Na_2O.	CaO.	FeO.	H_2O.	Total RO.	Fusibility.
Orthoclase	Tri-	64.7	18.4	16.9	.....	.....	.....	.....	16.9	5.0
Albite	Tri-	68.7	19.5	.....	11.8	.....	.....	.....	11.8	4.0
Oligoclase .	$\frac{3}{4}$ Tri-.... $\frac{1}{4}$ Bi-.....	61.0	24.0	2.0	9.0	3.0	.....	.....	14.0	3.5
Labradorite	Sesqui-	54.0	29.0	.....	5.0	11.0	1.0	.....	17.0	3.0
Anorthite .	Mono-.....	43.2	36.7	.....	.....	20.1	.....	.....	20.1	5.0
Kaolin ...	$\frac{2}{3}$ Mono-.. $\frac{1}{3}$ Bi-... .	46.3	39.8	.....	.....	.....	.....	13.9	.....	7.0

"From a study of this table it will be seen that the least silicious feldspar, anorthite, is the most infusible, while labradorite, one of the most aluminous, is the most fusible, which is the reverse of what would be expected from Bischof's formula; the latter feldspar, moreover, has 17 per cent of RO, as has also the least fusible feldspar, orthoclase, which shows that it is not a mere question as to the amount of RO or protoxide bases present."

The degree of fusibility or refractoriness caused by the alumina is governed 1st, by the greater or less reaction between the incorporated ingredients; 2nd, by the readiness of the alumina bearing ingredients to fuse; 3rd, by the readiness with which the most fusible element will become a liquid in which the other ingredients are more readily brought into combination with each other; 4th, by the physical condition of the ingredients.

There are at least two plausible reasons why an addition of 0.05 and 0.1 equivalent of kaolin to the Seger mixtures before quoted, and those given in my paper last year, makes the resultant mixture more fusible.

1. We know that clay when burned just sufficiently to accomplish dehydration becomes a Puzzolain material, *ie.*, when mixed with CaO, it will react with the lime making a Puzzolain cement, as do the Puzzolain slags and stones. This indicates that the anhydrous silicate of alumina formed, is in such a condition of chemical activity that it is capable

of uniting with other elements, especially calcium oxide, at a lower heat.

2. Carbonate of calcium mixed with clay begins to lose its carbon di-oxide below 800°C, as shown by the following data of heat of hydration:—

This experiment was made by Mr. A. V. Bleininger, on a mixture of carbonate of calcium plus 20 per cent. kaolin. The point when calcium oxide was found free in the mixture was noted by the heat evolved when it took on chemical water, forming calcium hydrooxide as in ordinary lime slaking, the heat evolved being measured in the calorimeter.

Degrees.	Calories.
500°	———
700°	———
800°	32.13
900°	126.43
1000°	128.52

This shows that combination between clay substance and caustic lime takes place below 800°, as at 800° we already have a considerable excess of calcium oxide as shown by heat evolved.

Bleininger also proved that kaolin is perfectly decomposed by caustic lime at 800° as was shown by all of its silica being removed by sodium cabonate solution.

Bleininger's experiments also showed that calcium carbonate when mixed with feldspar, begins to lose its CO_2 at 900°, and with free quartz at 925°. Thus it is shown that when calcium carbonate is mixed with clay, the clay becomes ready for chemical activity at a considerably lower heat than does the feldspar, due no doubt to the SiO_2 set free in a condition in which it most readily offers itself for combination with other elements.

Seger says[1] "Mixing substances ever so intimately will not be sufficient to induce combination. Chemical processes rather presuppose an unrestricted motion of the molecules, and never take place between two solid substances; one of these, at least, must be in a liquid or gaseous state. Hence, two solid substances will not produce chemical compounds,

1 Translation of the Collected Writings of Herman Seger, Vol. I, page 491.

unless a liquid is present that will dissolve one or both of them, and thus establish the proper contact."

This law of chemical reaction produced by the intermediation of a liquid or molten magma is not, in a ceramic mixture, *always* dependent *primarily* upon the fusibility of any one or more ingredients if taken alone. As has been shown in the case of clay and calcium carbonate, the reaction is facilitated or hastened by the chemical activity of the dehydrated clay.

Feldspar when fused, or in a liquid state, is capable of dissolving silica. A. Buenzli, (1876)[2] found with the aid of the microscope that at high temperatures, feldspar will dissolve a quantity of silica and that the amount of dissolved silica increased with the rise in temperature.

Then, if the carbonate of calcium has reacted on the clay at 800°, reducing it in a condition of chemical activity, and the feldspar has been reacted on at 900° and free quartz at 925°, it is plain to see that there is considerable silica in such a condition as to combine readily, forming silicates of the various bases present.

Fusion then, would be greatly accelerated by the action of the calcium oxide on the other ingredients; the more the calcium carbonate added (up to a certain limit) the earlier the fusion.

The general law governing this fluxing action is explicitly stated by R. T. Stull[2].

"Fusion or decomposition (of a fluxing mineral)may be brought about at lower temperature by the action of other substances upon it. This is generally the case of a flux acting upon a flux. In this way, a high fire flux may be made to exert its fluxing power at a temperature far below that at which it would otherwise occur."

It will be shown in the experiments to be given later, that while, in a Bristol glaze mixture containing no clay, the fusibility of the glaze is increased by increase of feldspar, greater fusibility is obtained by the introduction of clay up to a certain equivalent; and also that this increased fusibility

1 Translation of the Collected Writings of Herman Seger, Vol. I, page 507.
2 Trans-American Ceramic Society, Volume IV, page 255.

due to the addition of clay, is in proportion to the amount of calcium oxide present, thus showing that the reaction between the calcium carbonate and clay (two most refractory ingredients) does greatly facilitate and hasten the fusion, more so than would further addition of feldspar; also that by virtue of this reaction between the calcium carbonate and clay, glazes having 0.45 or 0.55 Eqv. of Al_2O_3 are the most fusible ones, providing the feldspar does not exceed 0.4 Eqv. This brings glazes carrying .55 Eqv. Al_2O_3 within the required range of fusibility of the average stoneware potter.

The extent to which the fusibility of the aluminous ingredient controls the fusibility of the whole mixture, is illustrated very clearly in cement manufacture. In all cement mixtures the chemical composition varies within very narrow limits. This narrow limit of variation in composition, according to all refractory quotients, and to popular opinion as well, should bring the finishing temperature of the clinker formation within very narrow limits of variation. Such, however, is not the case. It varies with the fusibility of the clay employed, the amount of clay substance proper, the fineness of sub-division of quartz, the presence or absence of feldspathic minerals, and the character of the carbonate calcium, whether crystaline or amorphous.

The fusion of a glaze mixture is not a function of temperature alone, but also of the manner of firing, the time given, and the form of the furnace, etc., as shown by Hecht[1].

Bristol glaze, No. XI, when burned on a green stoneware clay body in a majolica biscuit kiln, with gas, where the temperature was raised as rapidly as possible in 48 hours, fused to a beautiful white Bristol glaze at Cone 4. One of the managers of the company informed the writer later that in the glost fire at Cone 2, burned in 20 hours, this same glaze was a beautiful white glaze, perfectly matured. But when it was tried in a stoneware kiln, where the temperature was raised slowly with coal, it required Cone 7 to make it a good bright glaze.

The fuel used, whether gas or coal, makes a very appreciable difference in the results indirectly; but time taken to

1 Thonindustrie Zeitung, 1895, page 803.

mature the body and glaze, certainly has a direct and positive influence. Especially is this so in a Bristol glaze when zinc oxide is used in quantities ranging from 9.25 per cent. to 15 per cent. of the total batch weight.

In a fused Bristol glaze properly burned, the zinc is undoubtedly in three states (a) combined, (b) dissolved, (c) suspended in the glaze matrix The effect on the fusibilty of the glaze with the zinc in these various conditions, is obvious. In the first condition, its fluxing effect must be direct; in the second, slight, if any; and in the third, it cannot have any effect whatever.

From practical experience, the writer has learned that the longer the period of firing after fusion begins, the less opaque the Bristol glaze will be, showing that in the longer burn, more of the zinc is taken into the solution and combination.

Whether a Bristol glaze attacks the body sufficiently to cause a difference in the fusibility of the glaze on different bodies and in different lengths of time, I do not know.

S. Geijsbeek[1] cites a case where a glaze, the composition of which he did not know, but judged to be a zinc boro-lime glaze, did attack the white engobe to such an extent as to make the body of the ware plainly visible. But he says later, "Glazes generally used in stoneware potteries, high in alumina and silicic acid are usually well adapted for engobe purposes.

Langenbeck[2] has given the analysis of a glaze which had been used over an engobe; its chemical formula being

$$\left.\begin{matrix}0.26\ K_2O\\0.74\ CaO\end{matrix}\right\}\ 1.04\ Al_2O_3,\ 5.76\ SiO_2$$

He says, "In the severe fire (Cone 9 or 10) to which the ware has been subjected, the glaze has of course taken up alumina and silica from the engobe, so that its original composition would not accord, in the *proportion* of these elements, with the formula derived from the analysis of the fired products."

1 Transactions of A. C. S., Volume IV, page 53.
2 Chemistry of Pottery, page 145.

In this case, however, the RO elements and proportions are very different from those in the average white Bristol glaze. Therefore, it seems plausible that the attack of the glaze on the body, is not always governed by high proportions of alumina and silica in the glaze, as stated by Geijsbeek, but also upon the character of the RO fluxes involved.

It will be noted in the experiments to be cited later, that those cone mixtures in which the calcium carbonate is highest require a shorter period of time between starting to bend and going completely down, showing that when the fusion of the mass as a whole once begins, its action is rapid and violent. This same phenomenon is to be seen in brick clays high in lime. In the above glazes just given by Langenbeck, the calcium oxide is relatively very high, which unquestionably causes a rapid fusion similar to that noted in the instances just cited, thus creating a very solvent fluid, which if at all basic, would greedily attack the body, to an extent determined by the length of the burn and the temperature. But whether a Bristol glaze in which sufficient alumina and silica has originally been incorporated "to satisfy the glaze" as we say, and in which the lime is relatively low, will attack the body to any considerable extent is doubtful.

The ratio of alumina to silica to be used in a Bristol glaze is another factor governed by physical as well as chemical limitations. It is a well known fact that the average Bristol glaze can be softened by additions of silica, but the addition of the silica creates physical difficulties that the increase of fusibility cannot counteract, just as in the case of the feldspar before cited.

The writer has made no systematic experiments to determine the effect of various ratios between silica and alumina on various glazes, but has observed their effect in several cases.

Increase in the ratio between silica and alumina is always accompanied by a less opaque glaze, showing that more of zinc has gone into solution.

The writer has not had the privilege of making a microscopic examination of a burned white Bristol glaze, nor has

any record of such an investigation by anyone else been found. But it is probable that the opacity of the glaze, when high in alumina is due, in part, to the formation of crystals. But all the zinc cannot be said to be combined either in the fused portion of the glaze or in these crystals, but is free, either in solution or undissolved. When free, while it would not add to the opacity as much as it would if combined with the alumina, it does add its quotient to the opacity of the glaze. This is shown readily by the addition of more SiO_2 which reacts on the free zinc, taking it into combination with the other silicates.

The physical difficulty is noted in the "dusting" and "scaling" of the glaze high in flint.

The ratio between alumina and silica as found in the best glaze last year[1], *ie*—1 : 5 to 1 : 7, is born out by the following,—

A. S. Watts has given thirty-six porcelain body formulae[2]. He then remarks, "Only in two out of the thirty-six cases does the silica run below 3.7 and in only two cases of modern porcelain does it run over 6.0 SiO_2. As the formulae were figured with alumina as unity, these figures give the direct ratio. Porcelain mixtures are akin to Bristol glazes, the same general laws holding good in each case.

L. E. Barringer[3] found that the salt glaze he examined was essentially the same as could be used for stoneware, having the formula—

$$\left.\begin{matrix} 0.812\ Na_2O \\ 0.002\ K_2O \\ 0.182\ CaO \\ 0.002\ MgO \end{matrix}\right\} \left\{\begin{matrix} 0.612\ Al_2O_3 \\ 0.048\ Fe_2O_3 \end{matrix}\right\} 2.704\ SiO_2$$

In this case we find the ratio of alumina to silica to be 1 : 4.41+

Langenbeck[4] gives formulae of glazes analyzed by him as follows:

$$\left.\begin{matrix} 0.26\ K_2O \\ 0.74\ CaO \end{matrix}\right\} 1.04\ Al_2O_3,\quad 5.76\ SiO_2.\qquad \text{Ratio } 1 : 5.53$$

1 Transactions of A. C. S., Volume IV, page 73.
2 Ibid, 91, 92, 93.
3 Ibid, 213.
4 Chemistry of Pottery, page 145.

$$\left.\begin{matrix}0.3544\ K_2O \\ 0.6456\ CaO\end{matrix}\right\} 1.01\ Al_2O_3,\ 5.53\ SiO_2. \quad \text{Ratio } 1:5.47$$

$$\left.\begin{matrix}0.2335\ K_2O \\ 0.3660\ CaO \\ 0.4005\ ZnO\end{matrix}\right\} 0.3307\ Al_2O_3,\ 1.942\ SiO_2. \quad \text{Ratio } 1:5.86$$

The same author also gives the analysis and formula of two slip glazes as follows:

$$\left.\begin{matrix}0.1954\ K_2O \\ 0.4592\ CaO \\ 0.3454\ MgO\end{matrix}\right\} \left\{\begin{matrix}0.608\ Al_2O_3 \\ 0.081\ Fe_2O_3\end{matrix}\right\} 3.965\ SiO_2. \quad \text{Ratio } 1:6.52$$

$$\left.\begin{matrix}0.229\ KNaO \\ 0.020\ MnO \\ 0.2492\ MgO \\ 0.5015\ CaO\end{matrix}\right\} \left\{\begin{matrix}0.483\ Al_2O_3 \\ 0.078\ Fe_2O_3\end{matrix}\right\} 3.258\ SiO_2. \quad \text{Ratio } 1:6.7$$

Geijsbeek in his article "Red Glazes at High Temperature,"[2] quotes several workable alkali—alkaline earth glazes for Cone 8; whose ratio ranged from 4.5 to 5.15.

Seger[3] gives as follows, the formula of three clays which were used as slip glazes:

Glaze from Naumburg RO; 0.40 Al_2O_3; 2.30 SiO_2.
Glaze from Camenz RO; 0.68 Al_2O_3; 3.53 SiO_2.
Glaze from Dommitzsch RO; 0.80 Al_2O_3; 3.15 SiO_2.

The ratio of their alumina to their silica are respectively, 5.75, 5.09, 3.937.

A stoneware glaze made by G. Vogt,[4] and used on their stoneware exhibited by the Sevres Porcelain Works, at Paris Exposition, had the chemical formula of

$$\left.\begin{matrix}0.3\ K_2O \\ 0.7\ CaO\end{matrix}\right\} 0.32\ Al_2O_3,\ 2.02\ SiO_2. \quad \text{Ratio } 1:6.31.$$

The ratio of alumina to silica in glazes XI, XII, XIII and XIV before quoted, fall within the limits here indicated.

The following experiments were made to show the relative effect, in various mixtures, of the increase of feldspar at the expense of the carbonate of calcium; and the increase of clay in each case, as shown in the following epitome of the series.

1 Chemistry of Pottery, pages 146-92-84-85.
2 Transactions of A. C. S., Volume I, pages 62-65.
3 Translations of the Collected Writings of Herman Seger, page 453.
4 Volume —— Journal Society Chemical Industry.

Variations in Eqv. of K_2O	Each with a varying ratio of K_2O; Al_2O_3
.200	1 : 1.0
.250	1 : 1.2
.300	1 : 1.3
.350	1 : 1.4
.375	1 : 1.5
.400	1 : 1.6
.450	1 : 1.8
.500	1 : 2.0

Each of the above has an Al_2O_3: SiO_2 ratio of 1: 5.5 (except in the first numbers of each series, which are 1 : 6.)

Material used: Mayfield ball clay, Brandywine feldspar, ordinary commercial whiting, Goldings flint, and commercial zinc oxide were used in these tests. They were dried thoroughly before being used.

Mode of Manufacture: The first, second and last in each series were ground separately for one hour in a wet ball mill; screened through a 150 mesh sieve; dried to stiffness in plaster molds: and then to dryness over a hot plate and pulverized to pass a 40 mesh sieve.

For the intermediary members, aliquot parts of the second and last members of each series were mixed in dry condition by passing through a sieve several times.

The several mixtures were then made into cones. Each was worked up with water except the first member of each series. In these, sufficient dextrine paste was added (about 10 per cent.) to make the mass workable.

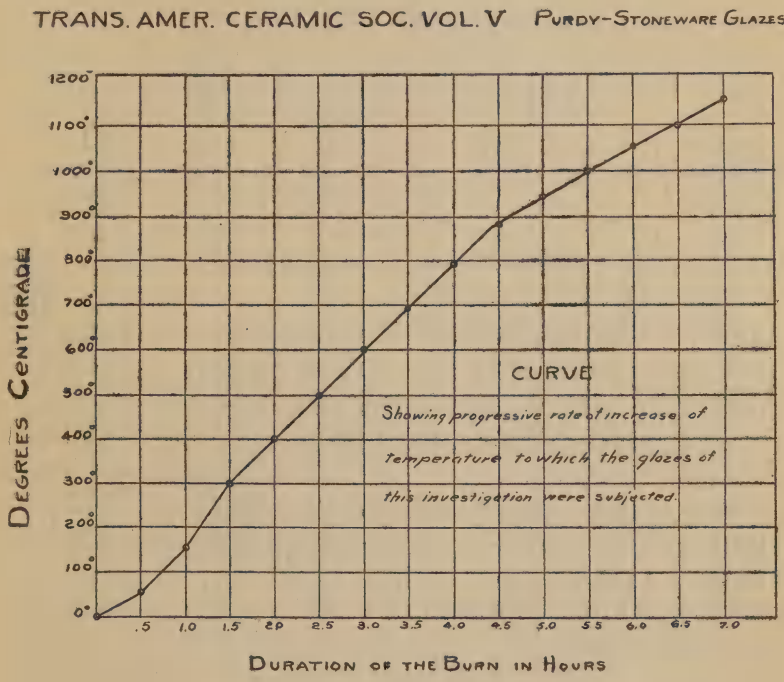
Burning: The burnings were made in an up-draught kiln in which a large muffle was used. The cone slabs were placed far enough to the rear of the muffle so as to prevent those nearest the open end flashing down.

The Le Chatelier pyrometer was used in connection with the Seger cones, to determine the temperature attained.

Series 1, 2, 3 and 4 were burned together on a slab in the first burn; 3, 4, 5 and 6 in the second burn; and 1, 2; 7 and 8 in the third burn, thus checking the pyrometer readings throughout the three burns. This was done because the pyrometer was used between times for several other purposes, the temperature reaching 1300° or more in each case. That the Le Chatelier pyrometer couples will suffer sufficiently by such treatment to differentiate the readings,

was proven by the readings obtained in the last burn. In this burn, the cones in series 1 and 2 came down 15° earlier than they did in the first burn, according to the readings of the pyrometer.

In each burn the following time—temperature curve was followed as closely as possible, after a reading of 120°C was reached, so as to insure similar conditions in each case. (See curve below.)



Stoneware Glazes—Series I. RO { 0.20 K_2O / 0.40 CaO / 0.40 ZnO

Glaze No.	Molecular Formula. RO	Al_2O_3	SiO_2	Ratio K_2O: Al_2O_3	Ratio Al_2O_3 :SiO_2	Fusing Temp. °Cent.	Proportions Blended.
I A	1.00	0.20	1.20	1:1.0	1:6.0	1150	I A alone
I B	1.00	0.24	1.32	1:1.2	1:5.5	1150	I B alone
I C	1.00	0.26	1.43	1:1.3	1:5.5	1135	7 parts I B—1 part I H
I D	1.00	0.28	1.54	1:1.4	1:5.5	1100	6 parts I B—2 parts I H
I E	1.00	0.30	1.65	1:1.5	1:5.5	1095	5 parts I B—3 parts I H
I F	1.00	0.32	1.76	1:1.6	1:5.5	1080	4 parts I B—4 parts I H
I G	1.00	0.36	1.98	1:1.8	1:5.5	1075	2 parts I B—6 parts I H
I H	1.00	0.40	2.20	1:2.0	1:5.5	1075	I H alone

Batch Composition of Extremes.

Ingredients.	I A	I B	I H
Feldspar	111.4	111.40	111.4
Whiting	40.0	40.00	40.0
Zinc oxide	32.4	32.40	32.4
Ball clay	——	10.32	51.6
Flint	——	2.40	36.0

Behavior in Fusing. — The cones of this series (I) went down so rapidly when they once started that they required close watching in order to note the time and temperature when they were fused flat, those higher in clay being the most rapid, due no doubt to the action of the CaO on the clay.

Appearance When Cooled. — The last four or IE, IF, IG and IH fused to clear glasses, while the first four IA, IB, IC and ID were semi-opaque, which is contrary to the rule that additions of Al_2O_3 to a glaze increase the opacity of that glaze.

Cone I A had a dead spongy appearance, which was less pronounced, in the others. as they increased in clay.

In this series each addition of ball clay made the mixture more fusible, the point of maximum fusibility not being reached.

Stoneware Glazes—Series II. RO { 0.25 K_2O / 0.35 CaO / 0.40 ZnO

Glaze No.	Molecular Formula. RO	Al_2O_3	SiO_2	Ratio K_2O: Al_2O_3	Ratio Al_2O_3 :SiO_2	Fusing Temp. °Cent.	Proportions Blended.
II A	1.00	0.250	1.50	1:1.0	1:6.0	1125	II A alone
II B	1.00	0.300	1.65	1:1.2	1:5.5	1150	II B alone
II C	1.00	0.325	1.78	1:1.3	1:5.5	1140	7 parts B and 1 part H
II D	1.00	0.350	1.92	1:1.4	1:5.5	1130	6 parts B and 2 parts H
II E	1.00	0.375	2.06	1:1.5	1:5.5	1130	5 parts B and 3 parts H
II F	1.00	0.400	2.20	1:1.6	1:5.5	1120	4 parts B and 4 parts H
II G	1.00	0.450	2.47	1:1.8	1:5.5	1115	2 parts B and 6 parts H
II H	1.00	0.500	2.75	1:2.0	1:5.5	1120	II H alone

Batch Composition of Extremes.

Ingredients.	II A	II B	II H
Feldspar	139.25	139.25	139.25
Whiting	35.00	35.00	35.00
Zinc oxide	32.40	32.40	32.40
Ball clay	———	12.90	64.50
Flint	———	3.00	45.00

Behavior in Fusing.—The cones went down rapidly after they once started.

Appearance When Cooled.—The cones showed their progressive fusibility from II H up to II B by their shape after being cooled. From II H to II D the melted cones were shapeless globules while II D showed semblance to cone shape, II C had round edges, and II B retained its shape and edges.

Stoneware Glazes—Series III. RO { 0.30 K_2O / 0.30 CaO / 0.40 ZnO

Glaze No.	Molecular Formula. RO	Al_2O_3	SiO_2	Ratio K_2O: Al_2O_3	Ratio Al_2O_3 :SiO_2	Fusing Temp. °Cent.	Proportions Blended.
III A	1.00	0.30	1.80	1:1.0	1:6.0	1100	III A alone
III B	1.00	0.36	1.98	1:1.2	1:5.5	1085	III B alone
III C	1.00	0.39	2.14	1:1.3	1:5.5	1075	5 parts B and 1 part H
III D	1.00	0.42	2.31	1:1.4	1:5.5	1045	4 parts B and 2 parts H
III E	1.00	0.45	2.47	1:1.5	1:5.5	1055	3 parts B and 3 parts H
III F	1.00	0.48	2.64	1:1.6	1:5.5	1060	2 parts B and 4 parts H
III G	1.00	0.51	2.80	1:1.7	1:5.5	1075	1 part B and 5 parts H
III H	1.00	0.54	2.97	1:1.8	1:5.5	1095	III H alone

Batch Composition of Extremes.

Ingredients.	III A	III B	III H
Feldspar	167.1	167.10	167.10
Whiting	30.0	30.00	30.00
Zinc oxide	32.4	32.40	32.40
Ball clay	——	15.48	61.92
Flint	——	3.60	41.40

Behavior in Fusing.—These cones behaved more normally, five minutes elapsing between the time they started and the time they were flat.

Appearance When Cooled.—They were all opaque white masses which showed nicely their order of fusibility; cone III D and III E being globules, while the others retained their shape more or less.

It is seen that in this series the point of maximum fusibility is reached when it contains .12 equivalent of clay, .15 equivalent, making the mixture but a trifle harder.

It was not expected that many of this series would fuse down before Seger cone 2 and as the plaque was rather crowded, only so many test cones were used as was judged necessary. So in comparison with Seger cones there was not as much data obtained as was desired. Cone 2, however, did not lose its sharp edges, although lying perfectly flat.

In this quick fire, cone III D or III E would make a good Bristol glaze, but not in the slow stoneware fires.

Stoneware Glazes—Series IV. RO { 0.35 K_2O / 0.25 CaO / 0.40 ZnO

Glaze No.	Molecular Formula.			Ratio	Ratio	Fusing Temp. °Cent.	Proportions Blended.
	RO	Al_2O_3	SiO_2	K_2O: Al_2O_3	Al_2O_3: SiO_2		
IV A	1.00	0.350	2.100	1:1.0	1:6.0	1075	IV A alone
IV B	1.00	0.420	2.310	1:1.2	1:5.5	1080	IV B alone
IV C	1.00	0.455	2.500	1:1.3	1:5.5	1045	3 parts B and 1 part F
IV D	1.00	0.490	2.695	1:1.4	1:5.5	1055	2 parts B and 2 parts F
IV E	1.00	0.525	2.887	1:1.5	1:5.5	1065	1 part B and 3 parts F
IV F	1.00	0.560	3.080	1:1.6	1:5.5	1090	IV F alone

Batch Composition of Extremes.

Ingredients.	IV A	IV B	IV F
Feldspar	194.95	194.95	194.95
Whiting	25.00	25.00	25.00
Zinc oxide	32.40	32.40	32.40
Ball clay	——	18.00	54.18
Flint	——	4.20	33.60

Behavior in Fusing:—The cones of this series were still more regular in their time of starting and melting flat, showing the effect of the decrease of carbonate of calcium.

While the most fusible of this series was flat on the plaque at the same temperature reading as III D, it had started five minutes earlier. At this part of the burn, the heat lagged a trifle below the time-temperature curve of the previous burn, thus allowing the cones to complete their coming down a trifle slower than they otherwise would. Their starting, however, was from five to ten minutes earlier than were those of series III, showing that IV C was really a trifle softer than III D.

Appearance when Cooled:—Cones IV B and D were globules while the others retained their shape more or less according to their fusibility. IV A and F appear to be equally fused, but IV F has a gloss, while IV A has only an incipient gloss.

In this series 0.105 equivalent of ball clay can be added before reaching its point of maximum fusibility.

Stoneware Glazes—Series V.

$$RO \left\{ \begin{array}{l} 0.375\ K_2O \\ 0.225\ CaO \\ 0.400\ ZnO \end{array} \right.$$

Glaze No.	Molecular Formula.			Ratio	Ratio	Fusing Temp. ° Cent	Proportions Blended.
	RO	Al_2O_3	SiO_2	K_2O: Al_2O_3	Al_2O_3 :SiO_2		
V A	1.00	0.375	2.250	1:1.0	1:6.0	1070	V A alone
V B	1.00	0.450	2.475	1:1.2	1:5.5	1045	V B alone
V C	1.00	0.487	2.681	1:1.3	1:5.5	1045	3 parts B and 1 part F
V D	1.00	0.525	2.887	1:1 4	1:5.5	1055	2 parts B and 2 parts F
V E	1.00	0.562	3.094	1:1.5	1:5.5	1065	1 part B and 3 parts F
V F	1.00	0.600	3.300	1:1.6	1:5.5	1090	V F alone

Batch Composition of Extremes.

Ingredients.	V A	V B	V F
Feldspar	208.87	208.87	208.87
Whiting	22.50	22.50	22.50
Zinc oxide	32.40	32.40	32.40
Ball clay	——	19.35	58.05
Flint	——	4.50	36.00

Behavior in Fusing:—The cones in this series were five minutes longer from the time they started to the time they were lying flat on plaque.

Appearance when Fused:—They resemble series IV very much, except that they show plainly that the point of maximum fusibility is approaching closer to the lower potash-alumina ratio, V B being considerably softer than IV B.

Stoneware Glazes—Series VI.

RO { 0.40 K_2O / 0.20 CaO / 0.40 ZnO

Glaze No.	Molecular Formula.			Ratio	Ratio	Fusing Temp. °Cent.	Proportions Blended.
	RO	Al_2O_3	SiO_2	K_2O: Al_2O_3	Al_2O_3 :SiO_2		
VI A	1.00	0.40	2.40	1:1.0	1:6.0	1065	VI A alone
VI B	1.00	0.48	2.64	1:1.2	1:5.5	1035	VI B alone
VI C	1.00	0.52	2.86	1:1.3	1:5.5	1045	3 parts B and 1 part F
VI D	1.00	0.56	3.08	1:1.4	1:5.5	1060	2 parts B and 2 parts F
VI E	1.00	0.60	3.30	1:1.5	1:5.5	1070	1 part B and 3 parts F
VI F	1.00	0.64	3.52	1:1.6	1:5.5	1095	VI F alone

Batch Composition of Extremes.

Ingredients.	VI A	VI B	VI F
Feldspar	222.8	222.80	222.80
Whiting	20.0	20.00	20.00
Zinc oxide	32.4	32.40	32.40
Ball clay	——	20.64	61.92
Flint	——	4.80	38.40

Behavior in Fusing:—Was similar to series V.

Appearance after Cooling:—While VI F seemed to be fused almost as much as IV F and V F, the other members of the series were more fused than the corresponding members of the other series, showing that this series was more fusible than V.

Stoneware Glazes—Series VII.

RO { 0.45 K_2O / 0.15 CaO / 0.40 ZnO

Glaze No.	Molecular Formula. RO	Al_2O_3	SiO_2	Ratio K_2O : Al_2O_3	Ratio Al_2O_3 : SiO_2	Fusing Temp. °Cent.	Proportions Blended.
VII A	1.00	0.450	2.70	1 : 1.0	1 : 6.0	1060	VII A alone
VII B	1.00	0.540	2.97	1 : 1.2	1 : 5.5	1050	VII B alone
VII C	1.00	0.585	3.22	1 : 1.3	1 : 5.5	1065	3 parts B and 1 part F
VII D	1.00	0.630	3.46	1 : 1.4	1 : 5.5	1080	2 parts B and 2 parts F
VII E	1.00	0.675	3.71	1 : 1.5	1 : 5.5	1085	1 part B and 3 parts F
VII F	1.00	0.720	3.96	1 : 1.6	1 : 5.5	1095	VII F alone

Batch Composition of Extremes.

Ingredients.	VII A	VII B	VII F
Feldspar	250.65	250.65	250.65
Whiting	15.00	15.00	15.00
Zinc oxide	32.40	32.40	32.40
Ball clay	——	23.22	69.66
Flint	——	5.40	43.20

Behavior in Fusing.—Very regular.

Appearance After Cooling.—This series, it will be noted, is quite a great deal harder than VI.

The gloss is good. The opacity or whiteness increases in depth with increase of alumina, but this increase in whiteness is accompanied with the same physical defects as was noted in glaze I, before given, when burned on the ware. Pin holes increase in number and size as the alumina increases. In fact, incipient crawling or drawing up into beads is very much in evidence in this series.

Stoneware Glazes—Series VIII. RO { 0.50 K_2O / 0.10 CaO / 0.40 ZnO

Glaze No.	Molecular Formula.			Ratio	Ratio	Fusing Temp. °Cent.	Proportions Blended.
	RO	Al_2O_3	SiO_2	K_2O: Al_2O_3	Al_2O_3 :SiO_2		
VIII A	1.00	0.50	3.000	1:1.0	1:6.0	1050	VIII A alone
VIII B	1.00	0.60	3.300	1:1.2	1:5.5	1060	VIII B alone
VIII C	1.00	0.65	3.575	1:1.3	1:5.5	1075	3 parts B and 1 part F
VIII D	1.00	0.70	3.850	1:1.4	1:5.5	1080	2 parts B and 2 parts F
VIII E	1.00	0.75	4.125	1:1.5	1:5.5	1095	1 part B and 3 parts F
VIII F	1.00	0.80	4.400	1:1.6	1:5.5	1120	VIII F alone

Batch Composition of Extremes.

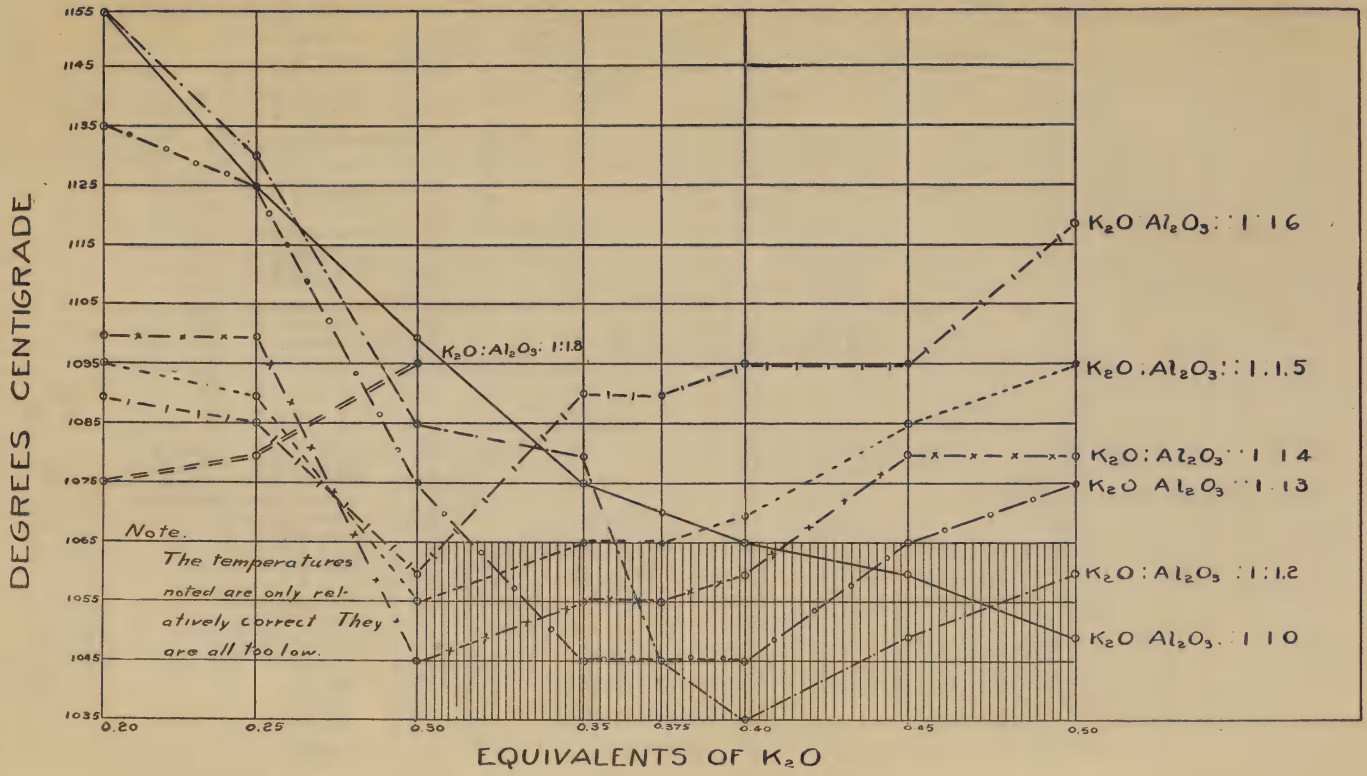
Ingredients.	VIII A	VIII B	VIII F
Feldspar	278.5	275.50	278.50
Whiting	10.0	10.00	10.00
Zinc oxide	32.4	32.40	32.40
Ball clay	——	25.80	77.40
Flint	——	6.00	48.00

Behavior in Fusing.—Very regular.

Appearance After Cooling.—All of this series except VIII A were very much pin holed. This pin hole phenomenon is not due to their refractoriness for they are fused to globules, but rather to their high content of feldspar and low content of whiting.

Curves have been drawn, to study these series as a whole, for the facts are thus more plainly shown. (See page 158.)

From these curves the formula of any of the mixtures can be readily figured. The zinc is retained at 0.4 Eqv. throughout; the potash is given on the abscissa; the calcium-oxide is then determined by difference, making (Eqv. K_2O + Eqv. ZnO + Eqv. CaO) = 1.0; the alumina in any mixture can be obtained by subsituting the equivalent of potash in the ratios which the curve represents, and upon which the mixture is described, and computing for the value of alumina; the silica in all cases is 5.5 times the alumina.


DEGREES CENTIGRADE
1155
1145
1135
1125
1115
1105
1095
1085
1075
1065
1055
1045
1035
0.20
0.25
0.30
0.35
0.375
0.40
0.45
0.50
EQUIVALENTS OF K2O
K2O : Al2O3 : : 1 : 1.8
K2O Al2O3 : : 1 1.6
K2O : Al2O3 : : 1 : 1.5
K2O : Al2O3 : : 1 1.4
K2O Al2O3 : : 1 1.3
K2O : Al2O3 : : 1 : 1.2
K2O Al2O3 : : 1 1.0
Note.
The temperatures noted are only relatively correct They are all too low.

The curves show:—

1st. That the most fusible glazes can be obtained with 0.30 to 0.4 equivalent of feldspar, 0.4 making the most fusible one.

2nd. That an increase of feldspar over 0.4 equivalents makes the glaze containing clay more refractory.

3rd. The series in which potash and alumina are as 1 : 1 shows that in each mixture without clay, increase of feldspar increases the fusibility, but as is shown in the following table, the lower the equivalent of feldspar, the larger can the potash-alumina ratio be before the fusing point reaches that of the glaze without clay.

TABLE XII

Showing that a high-feldspar glaze devoid of clay substance, melts at a higher temperature than one containing clay substance, and showing that as the amount of feldspar is decreased, the amount of clay substance must be steadily increased to maintain an equal fusing point.

Equiv. Feldspar.	Equiv. Al_2O_3 at which max. fusibility was attained.	Equiv. clay added for maximum fusibility.	Equiv. Al_2O_3 at which equal fusibility was maintained.	Equiv. clay added for equal fusibility.
0.500	0.50	0.00	0.50	0.00
0.450	0.54	0.09	0.54	0.09
0.400	0.48	0.08	0.56	0.16
0.375	0.4875 0.450	0.1125 0.075	0.5625	0.1875
0.350	0.405	0.105	0.515	0.165
0.300	0.420	0.120	0.540	0.240
0.200	Not reached	Not reached	Not reached	Not reached

4th. The glaze having 0.8 Eqv. of clay added with 0.2 Eqv. of feldspar, or K_2O, is as fusible as the glaze of 0.5 Eqv. of feldspar having only 0.3 of clay added. This is due, no doubt, to the action of the CaO on the clay. The CaO in the first instance amounts to 0.4 and only 0.1 in the latter.

5th. Figuring the equivalent of alumina in the glaze enclosed in the shaded rectangle, representing the most fusible glazes we have, in order of their fusibility for each equivalent of potash:—

TABLE XIII.

No.	K_2O	Al_2O_3	Equiv. of Clay	Temp. of Fusing
1	0.3	0.42	0.12	1045
2	0.3	0.45	0.15	1055
3	0.3	0.48	0.18	1065
4	0.35	0.455	0.105	1045
5	0.35	0.490	0.140	1055
6	0.35	0.525	0.175	1065
7	0.375	0.450	0.075	1045
8		0.4875	0.1125	
9	0.375	0.525	0.150	1055
10	0.375	0.5625	0.1875	1065
11	0.40	0.48	0.08	1035
12	0.40	0.52	0.12	1045
13	0.40	0.56	0.16	1060
14	0.45	0.54	0.09	1050
15	0.45	0.58	0.13	1065
16	0.50	0.60	0.10	1060

While these glazes thus tabulated fused considerably under Cone 2, and would give good glossy glazes at Cone 2 or lower, when burned in as short a period of time as this test was, they would require Cone 5-7 in the longer burns of the regular stoneware operations.

In order to verify the results attained in the foregoing investigation, the above sixteen formulae plus 2 per cent. "soluble salt" were given to stoneware potters to be tried as glazes under working conditions. Their percentage compositions are:

TABLE XIV.

Series No.	Distributing No.	Feldspar	Whiting	Zinc	Clay	Flint	"Soluble Salt"
III D	1	59.22	10.63	11.48	10.97	5.74	1.95
III E	2	56.36	10.12	10.93	13.05	7.59	1.96
III F	3	53.77	9.65	10.43	14.94	9.27	1.93
IV C	4	65.72	8.43	10.92	9.13	3.84	1.96
IV D	5	63.18	8.10	10.50	11.71	4.57	1.94
IV E	6	59.04	7.57	9.81	13.77	7.94	1.98
V B	7	71.00	7.70	11.25	6.60	1.54	1.98
V C	8	67.00	7.22	10.40	9.33	3.97	2.00
V D	9	63.25	6.85	9.87	11.80	6.17	1.98
V E	10	60.17	6.50	9.30	13.90	8.10	1.98
VI B	11	72.50	6.53	10.60	6.70	1.60	1.98
VI C	12	68.25	6.18	10.00	9.50	4.05	1.98
VI D	13	64.60	5.80	9.40	12.00	6.28	1.98
VII B	14	75.23	4.50	9.75	6.97	1.62	1.98
VII C	15	70.80	4.25	9.20	9.50	4.37	1.98
VIII B	16	77.50	2.77	9.00	7.20	1.67	1.95

By "soluble salt" was meant what ever the manufacturer was using to prevent crawling.

The Macomb Pottery Company, of Macomb, Illinois, Mr. Charles Kettron, manager, were not running at the time he received the formulae, but as they had a kiln of ware yet to set and burn, they hastily mixed the glazes up by hand, and screened them through a 100 mesh screen. Although imperfectly mixed, they showed very clearly their general behavior.

The heat, as shown by Seger standard cones as made by Prof. Orton, was Cone 7 about half down, Cone 6 having gone down but not flattened. Only in one place of the kiln was Cone 8 "tipped".

The gloss of all the trials was as good as could be expected from hand mixing.

The glazes which contained 0.52 equivalent Al_2O_3 or more, were the most opaque.

The trials were burned in the open, and on the inside of other ware; those burned in the open were a trifle more transparent; otherwise no material difference due to placing

could be noted. Sal-soda was used as the "soluble salt" to prevent crawling. English ball clay was used in all the trials.

Fortunately the trial pieces were half gallon pans which showed more clearly the effect of too high feldspar content than any other piece of stoneware could. Crocks, etc., are bunged, *i e*, placed one upon another allowing considerable space between surfaces, while the pans are nested, *i e*, placed one over the other, the one above resting upon the shoulder of the one below, thus making a comparatively close fit, and leaving but little space between surfaces. It is where the pans fit so closely that the glaze blisters or peels the most readily, that is, around the top edge of the inside and around the shoulder on the outside.

It has been the writers experience that glazes containing over 0.40 equivalent of feldspar, will thus blister when a glaze containing 0.40 equivalent of feldspar, or less, will not. The higher the content of the feldspar the more certainly will this blistering on the pans occur, and 0.50 equivalent of feldspar will invariably cause such blistering.

Another defect due to too high content of feldspar noted in these trials, is the crawling and beading up. Glaze 16 (VII B) was not only very badly crawled but also beaded up, and the inside edges of the pans were badly blistered. Glazes 14 and 15 (VII B and VII C) while not so badly crawled and beaded, were blistered around the inside edges of the pans. The other glazes, however. were practically free from such defects.

This crawling and beading up in glazes, high in feldspar and low in whiting has been noted in every case brought to the writer's attention, both in practice and in the experimental work by classes in the ceramic department, of the Ohio State University. It was even exhibited in the cones made of series VIII, as before noted.

Mr. George W. Shoemaker, chemist for the Robinson-Merrill Pottery Co. of Akron, O., ground the glazes for three hours in small ball mills; dipped them on bone dry ware, the glazes weighing between 24 oz. to 25 oz per pint; placed

them in open saggers in the lower and upper parts of the kiln (up draft, double deck.)

He used borax as the soluble salt; the clay used was china clay. They use Kentucky ball clay in their regular glaze, but Mr. Shoemaker claims to be having better success with this particular china clay.

The temperature attained, as shown by the cones, was very uniform throughout the kiln, cone six just touching the plaque in both top and bottom of the kiln, cone seven being but very slightly bent at the top and perfectly erect at the bottom. They fire the lower part of the kiln by coal in 58 to 60 hours, finishing the upper deck during the latter 10 hours of the burn by the aid of gas.

The trials thus burned in the gas fires of the upper deck were very much whiter than those burned in the coal fires, although the variations in gloss of the various glazes were the same in both parts of the kiln, showing the advantage of burning this type of glaze in purely oxidizing atmosphere.

None of the trials exhibited the crawling to the degree that those made up at Macomb did, due undoubtedly, to the thorough grinding they received.

Taken as a whole, all the glazes as prepared by Shoemaker, had good gloss, and opaqueness. The poorest one was as opaque as any to be seen on the market.

No. 16 or VIII	B	Very white, good gloss.
No. 15 or VII	C	Very white, good gloss.
No. 10 or V	E	But a shade darker than 15.
No. 13 or VI	D	
No. 14 or VII	B	
No. 3 or III	F	A trifle darker shade than the previous group, good gloss—considered fine white bristol glazes.
No. 4 or IV	C	
No. 5 or IV	D	
No. 6 or IV	E	
No. 8 or V	C	
No. 9 or V	D	
No. 11 or VI	B	
No. 12 or VI	C	
No. 1 or III	D	Still darker, but would be considered very good white bristol glazes.
No. 2 or III	E	
No. 7 or V	B	

The darkening of the shade, above referred to, is the decreasing of opaqueness, the yellow body showing through more plainly in the last group.

By comparing the percentage composition of the glazes the following facts are to be noted:

1st. The percentage amount of zinc used in the first group or 16, 15, 10, 13, 14, were 9.0, 9.2, 9.3, 9.4, 9.75 per cent. respectively as against 11.48, 10.93, 11.25 per cent. of the last and opaque group.

2nd. That this increase of opaqueness, notwithstanding the decrease in zinc, is due to the alumina is obvious. Comparing the average equivalents of alumina in the three groups, we have for the most opaque or group No. 1, 0.5685 Al_2O_3; for next groups, 0.4953 Al_2O_3; and for the next or least opaque 0.44 Al_2O_3. But is this increase of opaqueness between these three groups in proportion to the increase of alumina, and is it due entirely to this increase of alumina?

Comparing the average ratio of carbonate of calcium to clay in the three groups, we find for the first group 2.11; the second group, 1.43, and the third group, 1.04, *i. e.* for one part of whiting in the first group we have 2.11 parts of clay, etc. Thus, while the carbonate of calcium is decreasing in equivalents as well as in percentage amounts, there is an increase in the ratio of calcium carbonate to clay as well as an actual increase in content of feldspar.

A study of the fusion curve in the light of the experiment of Bleininger before quoted, shows the action of the calcium oxide in the several amounts. In series I with 0.4 $CaCO_3$ the maximum fusibility was not reached even with 0.16 equivalent of clay, and the fusibility of the mixtures decreased with the decrease of clay. Through the other series, this condition was being reversed regularly with decrease of $CaCO_3$ until in series VIII every addition of clay made the glaze more refractory.

In the case of glaze VIII B (16) the 0.1 equivalent CaO, has "spent" itself upon the clay leaving, possibly, some clay undecomposed to play its role as a refractory ingredient, the feldspar being the principal solvent medium.

As has been pointed out, mixtures in series VIII were very steady and slow in fusing, indicating a less active fluxing condition. Therefore more zinc would remain uncombined, and the glaze composition would be that of the slightly

opaque potash-alumina-silicate instead of the clear lime-zinc-alumina-silicate as in the case where sufficient CaO is present to decompose all the clay.

The answer then to the query of why, as the feldspar increases, less clay can be added before raising the fusibility of the mixture is, that with the increase of feldspar there is a decrease of $CaCO_3$ the active agent in the decomposition of the clay and feldspar, which renders them in a condition for more ready fusion.

The effect of too high content of feldspar in the Akron trials, was not so much in evidence as in the trials from Macomb, due probably to the more thorough grinding. Yet, 16 (VIII B) was crawled and had incipient blisters.

Of the various mixtures tried 13, (VI D) is the most successful and economical glaze, and its formula 0.4 K_2O, 0.2 CaO, 0.4 ZnO, 0.56 Al_2O_3, 3.08 SiO_2 would be the one recommended for stoneware at Cones 6-7. For higher heats the Al_2O_3 and SiO_2 can be increased, always keeping their ratio 1 : 5.5; for lower heats the Al_2O_3 and SiO_2 can be decreased, but never below 0.48 Al_2O_3, always keeping the ratio of Al_2O_3 SiO_2, 1 : 5.5.

DISCUSSION.

Mr. Stanley G. Burt: I would like to ask, in this series of Bristol glazes, whether the lower-fusing formulae retain their opaqueness?

Mr. Purdy: I expect they will. The opaqueness, as I stated last year, is due, in part, to alumina, and it was questioned whether so much alumina as 0.5 could be retained, and not affect materially the fusibility of the glaze. In my paper last year, there were several formulae given in which zinc was higher than four-tenths. These glazes when made up and fired, crawled, and when made lower than that in zinc they were not white. I, therefere, chose four-tenths zinc. Four-tenths zinc, however, will not cause opacity when the alumina is less than 0.40, and further addition of alumina increases the opacity. Therefore, I believe we are safe in assuming that these lower-fusing formulae will retain their opaqueness.

Mr. Burt: Your white means opacity?

Mr. Purdy: Yes, sir.

Mr. Burt: I think it would be interesting to have one not showing opacity. It is a question whether we haven't there the making of a clear leadless glaze.

Mr. Purdy: An addition of five hundredths of lime at the expense of the zinc will clear the glaze up.

The Chair: Did you ever try to replace the zinc with oxide of tin for whiteness?

Mr. Purdy: Yes, sir. I would like to have some one explain to me why, with four-tenths of an equivalent of feldspar, we have the most fusible glaze, and why any addition of feldspar above that point makes it more refractory? With this four-tenths equivalent of feldspar, we have also two-tenths lime, which, with the four-tenths zinc makes up the RO.

The Chair: What is the amount of the lime in those glazes where you increase the feldspar and which become more refractory?

Mr. Purdy: In these trials, lime was not added in sufficient quantity to have refractoriness due to the excessive lime. But we do have refractoriness when the spar is increased *at the expense of* the lime.

The Chair: It may be a little like adding lime as a flux in a vitreous body. It helps to bring the body to vitrification up to a certain point, but an increase of lime above that, goes the other way again.

Mr. Langenbeck: I think Mr. Purdy's paper is extremely interesting on account of the side lights it has thrown upon the behavior of glazes under different conditions of firing in general; particularly his observation of the maturing of some of the glazes of this series at a lower temperature under rapid fire, than in a regular kiln in which there is a large mass of ware. A great many must undoubtedly have been puzzled as I have, by the apparently radical difference in behavior of glaze trials in a small experimental furnace and in a large kiln. And I think, furthermore, that his observations on the conditions under which clay and lime are brought into chemical activity are of far-reaching import,

not only in glazes, but in fluxing bodies for vitrification; it seems to me, it would be an interesting starting point for many different lines of experiment. I know in a general way, of course, that the relations of feldspar to alumina and silica, with reference to vitrification and after fusion, vary very strangely according to proportions. We know this in a general way from Seger's experiments along this line; but I don't know at all, even with the amount of work done, and the contributions which Mr. Purdy has added, that any theory yet can be developed—I don't know of anyone who can answer Mr. Purdy's question to explain why the increase of feldspar beyond four-tenths equivalents causes the body to become more difficult to fuse. Undoubtedly there is a law, and when we get the many facts together; we can develop the law which will be a guide to future work. The idea that an increase of basic elements necessarily increases fusibility at the same time, was long ago upset.

If you take the case of vitreous porcelain bodies, it is frequently desirable to increase the fusibility of the body, and for practical reasons you must have a certain amount of clay present in order to produce a workable, sufficiently plastic mass. But since your feldspar already carries so much alumina with it, you must reach your alumina and silica with some more fusible flux. It doesn't make a particle difference whether the flux is more fusible than feldspar; its combination with clay is much more fusible than you can make it with any feldspar addition. And I would like to say in that connection, that the ordinary method of guaging the fluxing properties of feldspar which the potter uses, viz., putting it in the kiln and seeing how it fuses in comparison with other spars, is incorrect. The assumption that because one flux is more fusible than another *per se*, it follows that the use of the more fusible flux is going to make a body more fusible, is not necessarily the case. Mr. Purdy's experiments demonstrate that.

FURTHER CONTRIBUTIONS TO THE MANUFACTURE OF ARTIFICIAL SANDSTONE OR SAND BRICK.*

BY

S. V. PEPPEL, B. Sc., COLUMBUS, O.

This contribution is the result of work carried out to determine the allowable impurities in raw material and the conditions of manufacture which will produce the best sand-brick. I would suggest that the use of the term "sand-brick" be limited to those bodies which consist of a mass of sand particles bound together by a net work of calcium-, calcium-magnesium-, or magnesium-silicate, formed by the action of steam under pressure upon silica or quartz and calcium or magnesium hydrates or a mixture of both of them.

Illustration No. 1, shows the fractured surface of such a body, enlarged eight diameters.

In any industry, and especially in a young one, there are always many questions which are the occasion of a great deal of uncertainty both in selection of raw materials and machinery for manufacture. When an industry has got well started, we know that with certain raw material, handled in a definite manner, in a certain machine or combination of machinery, certain desirable results can be accomplished. We also know that a certain raw material exactly like in every respect to that in use, is not always available, or if available there may be something else of little value for any other purpose, which could be just as well used, and sometimes with better results. And farther, it frequently happens that the first machines in use are not the most economical, or do not produce the best possible product.

It was to settle as many of these questions as possible that the work which I am about to report upon was instituted. We set out with a view of determining the effect of the ordinary impurities in the class of materials which in a comparatively pure state, has been used in the manufacture of sand-brick and to learn what was required of each machine,

*Published in advance, by permission of Professor Edward Orton, Jr., State Geologist of Ohio.

SHOWING THE FRACTURE OF A SAND BRICK
ENLARGED 8 DIAMETERS.

with a view to pointing out their faults, if any could be found.

In order to do this, it was necessary to establish an artificial stone factory, on a small scale, so constructed that we could control the working conditions exactly. The forms into which our product was made were only two, one having the shape of the ordinary cement brickette to be used in determining tensile strengths, and a two inch cube for testing the crushing strength. We had cast-iron molds and dies made for producing these two shapes, expecting to use a hand brick press for the necessary power. For a cylinder in which to harden the brick, we used a piece of ten inch wrought-iron pipe, fitted up with flanges and cast-iron heads on each end. For steam pressure we had access to a 100-horse power boiler, capable of carrying steam up to 250 pounds pressure.

Although we thought this outfit ample and satisfactory for experimental work, we soon found our troubles.

After a few trials, had to abandon the hand press, since we could neither get pressure enough nor control the pressure uniformly. We surmounted this difficulty by placing our dies between the heads of a Tinius Olsen 100,000-pound testing machine, where we could not only give as much pressure as we wanted, but could also control every movement and record exactly what we were doing.

We will take up the discussion of the subject under six heads, although in the nature of the case the working out of the problems under each head interlocked and overlapped each other at many points. The facts fall naturally under the following heads:

1. The raw material and its preparation
2. The behavior of the mixture in the press.
3. Hardening.
4. Testing.
5. Mechanical equipment.
6. Discussions of the merit of the various systems, including patents.

I—THE RAW MATERIAL AND ITS PREPARATION.

As before stated, the sand-bricks consist of a mass of sand particles bound together into a rocklike structure by a network of lime or magnesium silicates. The raw materials consist of only two principal substances, the sand and the quicklime. They will be discussed in turn.

A—THE SAND.

First. Almost any sand *can* be used, and fair product produced, if the treatment is properly varied to suit the physical and chemical properties of the sand. Economy in manufacture, however, limits both physical and chemical properties.

While a good-appearing brick, moderately strong at the time it is taken from the hardening kettle, can be made from almost any kind of sand, still for a safe and durable material of construction, there are certain limitations in the chemical, or rather mineralogical make-up of the sand, aside from those dictated by economy in manufacture, as will be shown later by experimental results. A sand with too much clay in it will make a brick which will not stand up long under the attacks of severe weather.

Second. A comparatively pure sand is essential to cheap manufacture, as well as for the production of a safe and durable material, nor should the sand be too coarse. For the best results it is probable that most of it should pass through a screen, 20 meshes to the inch, unless there is a good gradation from coarse to fine particles, in which case a coarser sand might be used.

Since sand constitutes the major portion of the raw material for this industry, we will take up the examination of it first.

Beginning with comparatively pure sand, the first problem is, what proportions of coarse and fine sand are best. Work done by Prof. Glasenapp showed that some fine sand is necessary. Dr. Michaelis has said that two-thirds coarse sand and one-third fine give the best results. This statement, of course, is a little indefinite, since coarse and fine sand are not defined. Reason tells us that the mixture

which will leave the smallest amount of interstitial space when pressed together, will be the best. This might be calculated exactly. But since such a sand would not be attainable in a commercial way, the calculation is omitted, and practical tests will be given to show the effect of varying amount of very fine sand.

In all the work which follows a pure, sharp glass-sand was used. On giving it a mechanical analysis, it was found to be made up of the following sizes:

20 to 40 mesh—50%
40 to 60 mesh—33%
60 to 80 mesh— 7%
80 to 100 mesh— 7%
100 to 120 mesh— 2%
120 to 150 mesh— 1%

Since this sand showed no very fine grained particles, they were supplied in the form of a pure potters flint. The mechanical analysis of the flint was as follows:

100 to 120 mesh—0.70%	Sieve Separation.
120 to 150 mesh—1.00%	
150 to 200 mesh—1.25%	
.00212 in. diam.—24.00%	Sedimentation Separation.
.00086 in. diam.—19.00%	
.00040 in. diam.— 8.50%	
.00026 in. diam.— 7.50%	
.000136 in. diam.— 5.70%	
Too fine for measurement—32.55%	

Both sands were practically free from soluble silica.

In order to test the influence of the different proportions of the two sands, a series of cubes and brickettes were made up and hardened. All the conditions of manufacture were maintained as nearly uniform as possible. Five per cent. caustic lime and five per cent. of water above that needed for hydration were used. The lime used in these tests was steam slaked. The results here given are the average of three tests of each kind:

TABLE I.

Number	Composition.		Crushing Strength Pounds per sq. inch.	Tensile Strength Pounds per sq. inch.
	Parts Coarse.	Parts Fine.		
77	8	2	3114	131
79	4	2	2955	144
84	3	2	2461	224

These results are very instructive and clearly indicate that much more work might well be done along this line.

It is evident from the above figures that a decrease in the proportion of the coarse sand, decreases crushing strength, and that it increases tensile strength. While this is the case for the range of mixtures examined, I think when carried further, limits will be reached in both directions, and I regret very much that we are unable, at present, to fix these limits.

The blocks for the preceding test were made in the hand brick machine, on which it was impossible to give each block exactly the same pressure as the last. Since, as we shall show later, the pressure in making has a decided influence on the strength, the above results would probably show a close relation between the decrease in crushing strength and the increase in amount of very fine particles, if they had been made in a machine where this pressure was under accurate control.

From the foregoing I would conclude that in order to maintain the best conditions, and using a sand all of which would be retained on a 40 mesh screen, we should have to grind one-fourth of the sand so that at least one-half of it would pass a 150 mesh screen. If, however, we had a sand with a good assortment of sizes from coarse to fine, we ought to have sand finer than 150 mesh at least equal in amount to the weight of lime to be added.

The fine sand not only fills the spaces between the coarser particles, but assists in the even distribution of the lime, and very much accelerates the chemical reaction so necessary to strength.

ORDINARY IMPURITIES.

The ordinary impurities in sands are for the most part silicates, represented by clay, mica, feldspar, etc., and almost always some ferric oxide. Mica and feldspar are frequently absent, but clay and oxide of iron are seldom absent entirely. While in the general run of cases, feldspar and mica are not present in any important quantity, there are regions in which the sands are rich in one or the another, and sometimes

in both. Oxide of iron, which is almost always present in greater or less quantity, reacts with silica very slowly, if at all, in the presence of steam under pressure; it may therefore be considered inert except for its coloring action, unless it acts as a promoter of chemical combination, as is the case with ferric oxide in the manufacture of Portland cement. No attempt was made to determine whether this is the case or not. By far the most wide spread impurity in sand is clay, or kaolinite. If there is any impurity in sand, clay is nearly always there, and there are many sands which carry considerable quantities of clay. Its effect on the sand-brick process was therefore studied in more detail than that of any of the other impurities.

No tests were made with mica, since it would seldom be found in sufficient quantity in sand to extend much of an influence. Prof. Rinni,[1] of Hanover, commenting on the examination of a number of sections under the microscope, says: "Mica flakes do not seem to have been materially attacked. Quartz and feldspar do not show much if any difference."

The Influence of Kaolin, as an Impurity in Sands.

The action of kaolin was examined as representing the hydrous silicates like clay, and feldspar as representing the more complex anhydrous silicates.

The experimental series of mixtures designed to test the influence of clay as an ingredient of sand are set forth in the following tables II to VI. The mixtures were made up into cubes and tensile test pieces in each case, in as uniform a method as possible.

In Tables II and III, five per cent. of the same lime was used in each case, but in Table IV, five per cent. of a different lime was used. In Tables II and IV the ratio of coarse particles to fine particles in the sand mix was 4 to 1; and in Table III, 3 to2. In Table V the coarse to fine was 2 to 1, and ten per cent. of lime was used; in Table VI, 2 to 1, and ten per cent. of dolomite; thus, the tables are not strictly comparable with each other. However, in each table, the only variable is the amount of kaolin which was used to

1 Thon Industrie Zeitung, 1903, No. 16, p. 153.

replace the flint or fine material. Tables V and VI are the averages of a comparatively large number of tests.

TABLE II.

Data:—Molding Pressure—10000 pounds per square inch.
Steam Pressure—150 pounds per square inch.
Temperature in Hardening Cylinder—185°C.
Time Exposed to Steam—10 hours.

Number of Test.	Composition of Mixtures.					When Tested.						Per cent. water absorption.
	Parts Coarse Sand	Parts Fine Sand. (Including impurities.)	Percents Kaolin.	Per Cent. Qu'ckl'me		At once after hardening		After ageing		After freezing		
				Pure CaO	Dolomitic	Crushing Strength	Tensile Strength	Crushing Strength	Tensile Strength	Crushing Strength	Tensile Strength	
85	4	1	2.5	....	5	2766	338	2449	194	2917	219	8.32
86	4	1	5.0	....	5	2500	210	2376	277	2481	181	8.00
87	4	1	10.0	....	5	1943	184	1687	157	1910	121	8.50
88	4	1	20.0	....	5	1705	162	1325	138	1477	93	9.00

TABLE III.

83	3	2	...	...	5	3697	427	....	....	3812	215	8.06
89	3	....	2	....	5	2260	238	1846	187	2117	156	10.36

TABLE IV.

93	4	1	2.5	5	....	3835	351	3955	364	4502	352	8.62
94	4	1	5.0	5	....	3340	295	3342	175	3887	269	8 60

TABLE V.

Data:—Molding Pressure—15000 pounds per square inch.
Steam Pressure—150 pounds per square inch.
Temperature in Hardening Cylinder—185°C.
Time Exposed to Steam—10 hours.

Number of Test.	Composition of Mixtures.					When Tested.						Per cent. water absorption.
	Parts Coarse Sand	Parts Fine Sand. (Including impurities.)	Percents Kaolin.	Percent Qu'ckl'me		At once after hardening		After ageing		After freezing		
				Pure CaO	Dolomitic	Crushing Strength	Tensile Strength	Crushing Strength	Tensile Strength	Crushing Strength	Tensile Strength	
A*	2	1	....	10	....	7745	437	.....	.....	9007	371	8.62
C†	2	1	10	10	....	5872	593	.....	.....	6194	561	6.41

*A is the average of tests Number 106, 107, 108, 109, 110 and 111.
†C is the average of tests Number 118, 119 and 120.

TABLE VI.

B*	2	1	....	....	10	5187	286	.....	....	5853	314	9.11
D†	2	1	10	..	10	4429	445	.....	.....	4818	459	8.05

*B is the average of tests Number 112, 113, 114, 115, 116 and 117.
†D is the average of tests Number 121, 122 and 123.

TABLE VII*.

89	3	....	2	....	5°	2260	238	1846	187	2117	156	.....
92	3	...	2	....	20	4729	599	3780	596	5797	480	.....
83	3	2	....	....	5	3697	427	.....	.....	3812	.....	.....
90	3	2	....	....	10	5607	503	5843	446	7525	417	.....

*Conditions of manufacture same as Table III.

Reviewing the facts expressed in tables II, III and IV, where the brick are made under a pressure of 10,000 pounds per square inch, we observe that with each addition of kaolin there is a marked decrease in both tensile and crushing strength, this being most marked in table III, where in test 83 the proportion of flint was large and in test 89, where all of this flint was replaced by kaolin. Also we observe that the decrease in crushing strength is at least one-third with the addition of 20 per cent. of kaolin.

Tables V and VI, the blocks for which were made under

a pressure of 15,000 pounds per square inch, tell a different story. Here again with the addition of kaolin, there is a marked falling off in crushing strength, accompanied by a very decided increase in tensile strength. The effect of the pressure used in molding the block will be discussed under pressing.

Coming back to tables II and III, we observe number 88, 20 per cent. kaolin, shows a very decided loss in strength after the freezing test, as well as on ageing for 35 to 40 days. This is also the case with number 89, which is very rich in kaolin.

The increase in strength shown here as due to freezing, will be discussed in connection with the effect of frost in general on all kinds made.

It was next thought that an increase in lime might overcome the ill effects of a large amount of kaolin, and to test this number 92 was prepared and made under the same conditions as number 89, except that 20 per cent. of lime was added instead of five per cent. This test proved that an increase in lime did in a measure counteract the influence of high kaolin. In comparing figures in table VII, it will be noted that between 89 and 92 there is a marked increase in strength, the tensile strength being more than doubled, and that after the freezing test, number 92 shows an increase in crushing strength when number 89 shows a decrease. However, going farther and comparing numbers 83 and 90 in which there is no kaolin, and in which the lime was only increased from five to ten per cent., we see that there is approximately as much increase in strength for the addition of ten per cent. here, as there was with 20 per cent. in the preceding case where kaolin was a large part of the mixture. Another very pertinent point to be observed is that the increase in strength after freezing is very much greater in the case of numbers 83 and 90 than it is with 89 and 92.

So that while an increase of lime does in a measure overcome the bad effect of clay in large amount, we are safe in saying that any considerable amount of clay in a sand to be used in this industry, is very undesirable, since to use enough lime to make it a safe product, would make it too

expensive, and after all the product would not be the best.

From the preceding facts it would appear that clay up to ten or twelve per cent. is probably not dangerous, and possibly as small an amount as two and a half per cent. might be desirable.

Clay adds to the ease in molding. Owing to its smooth unctuous nature, it acts as a lubricant and decreases the friction on the mold.

The influence of feldspathic minerals as an ingredient of sand.

The effect of feldspar was not examined in the same detailed manner that kaolin was, since it is not so common an ingredient, in quantity. However, a number of blocks composed of sand containing ten per cent. of fine feldspar were made, using a pressure of 15,000 pounds to the square inch. The average result of all the tests on this are given under F in Table VIII. The tests grouped under B are parallel in every way, except that no feldspar was introduced into the sand.

TABLE VIII.

Data:—Molding Pressure, 15000 pounds per square inch.
Steam Pressure, 150 pounds per square inch.
Temperature in Hardening Cylinder, 185°C.
Time Exposed to Steam, 10 hours.

Number of Test.	Composition of Mixtures.					When Tested.						
	Parts Coarse Sand.	Parts Fine Sand (Including Impurities.)	Per Cent. Feldspar.	Per Cent Qu'ckl'me		At once after Hardening.		After Ageing		After Freezing.		Per Cent. Water Absorption.
				Pure CaO.	Dolomitic.	Crushing Strength.	Tensile Strength.	Crushing Strength.	Tensile Strength.	Crushing Strength.	Tensile Strength.	
B*	2	1	0	....	10	5187	286	.....	.....	5853	314	9.11
F†	2	1	10	..	10	4619	339	.....	.....	5115	197	6.94

*B's the average of tests number 112, 113, 114, 115, 116 and 117.
†F's the average of tests number 124, 125 and 126.

Studying Table VIII we note a slight decrease in crushing strength, and an increase in tensile strength, between B and F. After freezing, F increases in crushing strength, but not at the same rate as B. The only erratic factor in

the series is the marked falling off of the tensile strength after freezing.

On the mechanical tests alone we would hardly be justified in excluding a sand which carried as much as ten per cent. feldspar. However, from a few preliminary experiments, I know that both quicklime and caustic magnesia react on feldspar to some extent when exposed to steam at 150 pounds pressure for ten hours, and this reaction can hardly happen without the liberation of potassium or sodium salts and since the solubility of all the salts of these metals is so well known, the danger of effloresence or scumming from this source would be great, if any appreciable amount of the feldspar were attacked by the lime. Until it is definitely proven that feldspar in lime-sand-brick does not produce scumming, I should be cautious about using such a sand, if I desired a first-class product when working at high steam pressure.

If, on the other hand, the feldspar molecule opened up, and took on calcium-oxide and silicic acid, (SiO_2) making a more complex and insoluble silicate, there would be no danger of scumming, and we should have a stronger brick for each unit of calcium-oxide used. The results tend to show that this complex silicate is not built up, since the brick with feldspar were slightly weaker, rather than stronger.

A preliminary experiment made at 150 pounds steam pressure and ten hours time showed quartz to be more attacked by lime than feldspar was. From this we might infer that sands rich in feldspar could safely be worked, by keeping the steam pressure down to 120 pounds or lower, and by not allowing the bricks to remain in the cylinder any longer than necessary to get enough quartz into combination to produce a good bond. Working in this way it is probable that not enough feldpars would be broken up to give any trouble later.

The influence of soft-burnt clay as an ingredient of sand.

On account of the hydraulic properties developed by mixtures of weakly-ignited clays and caustic lime under ordinary atmospheric conditions, it was considered advisable

to test their behavior under high pressure steam. As can be readily seen from Table IX, nothing would be gained by the use of dehydrated kaolin, since the blocks made with fine sand under the same conditions of manufacture developed double the strength shown when dehydrated kaolin is used.

TABLE IX.

Data:—Molding Pressure, 15000 pounds per square inch.
Steam Pressure, 120 pounds per square inch.
Temperature in Hardening Cylinder.—180°C.
Time Exposed to Steam, 8 hours.

Number of Test.	Composition of Mixtures.					Tests.	
	Parts Coarse Sand.	Parts Fine Sand (Including Impurities.)	Parts Burnt Kaolin.	Per Cent. Quicklime.		Crushing Stength	Tensile Strength
				Pure CaO.	Dolomitic.		
A 8	2	1	.....	10	.....	8545	.....
I 8	2	.....	1	10	.....	3919	459
B 8	2	1	.....	.....	10	6038	.....
J 8	2	.....	1	.....	10	3110	256

This concluded the work on the impurities of the sand.

While it was very probable indeed that sharp sands are much to be preferred, I regret that we have no comparative tests to show just how much difference the shape of the grains will affect the strength of the material produced.

B—THE QUICKLIME.

The work of Prof. Glasenapp, cited by us in an article "The Manufacture of Artificial Sandstone", in Volume IV, of this society's transactions, showed the necessity of at least a small amount of very fine sand in order that the chemical reaction may not be too much retarded by lack of intimate contact between sand and lime particles. This brings us to a consideration of the lime.

Quantity Required.

Naturally, the first query is as to quantity. Practice ranges from five to ten per cent. In order to determine the desirability of using large or small amounts of lime, it was

necessary to find out if the strength increased with an increase of lime, and if so, whether the increase was proportional to the increase in lime. To get these facts the following series of test were made, as shown in Table X.

TABLE X.

Data:—Molding Pressure, 10000 pounds per square inch.
Steam Pressure, 150 pounds per square inch.
Temperature in Hardening Cylinder, 185°C.
Time Exposed to Steam, 10 hours.

Number of Test.	Composition of Mixtures				When Tested.						
	Parts Coarse Sand.	Parts Fine Sand (Including Impurities.)	Per Cent. Quicklime.		At once after Hardening.		After Ageing		After Freezing		Per Cent. Water Absorption.
			Pure CaO.	Dolomitic.	Crushing Strength.	Tensile Strength.	Crushing Strength.	Tensile Strength.	Crushing Strength.	Tensile Strength.	
83	3	2	....	5	3697	427	....	....	3812	....	8.06
90	3	2	....	10	5607	503	5843	446	7525	417	9.87

TABLE XI.

84	3	2	5	....	2636	194	....	....	....	....	10.25
97	3	2	40	....	7018	541	7153	622	7995	516	12.13

Studying Tables X and XI, we see in Table X, where dolomite lime was used, an increase in strength with an increase in lime, and also that while the lime was doubled, the increase in strength was only a little over 50 per cent. After freezing, the sample containing the increased lime does show almost 100 per cent increase in strength. However, this increase is probably mainly due to the changing of free lime into carbonate, by the carbonic acid in the water which was used to thaw out the bricks after each freezing.

In Table XI, a high-calcium lime was used, and extremes of high and low lime were compared, using eight times as much in number 97 as was used in number 84. With an eight-fold increase of lime, only a three-fold increase of strength was produced

We might then conclude from the foregoing, that while there is an increase in strength with an increase in lime, this

increase is less marked the higher the lime becomes, and that the strength gained by the addition of lime beyond ten per cent. would not justify the additional expense. Therefore, we may say that present practice in this respect is very good.

It should be stated here that the percents of lime given in this paper are all based on the raw sand as unity. That is, five per cent. lime means that five pounds of lime was added to 100 pounds of sand.

Pure vs. Dolomitic Limes.

Having decided how much lime we should use, the next question which presents itself is whether some particular type of lime will serve our purpose better than any other? Will a hydraulic lime be as good or better than a pure lime? Will lime made from dolomite be as good as one made from a high-calcium limestone?

In view of the facts shown in Table IX, that lime and dehydrated kaolin do not develop any strength under high pressure steam, we would infer that steam under pressure is not conducive to the development of the hydraulic properties of a hydraulic lime. We would therefore expect that the calcium-silicate of such a lime would be inert so far as developing immediate strength in a sand-brick is concerned. This may be due to the dearth of moisture, since hydraulic lime is best in wet places. The hydraulic properties of a lime might develop slowly in the brick after manufacture, and at the end of a year show great strength, especially if the brick were in contact with water. This is, however, an open question as yet.

We naturally consider pure limes the best, if carefully burned, since for each unit of weight we have available a greater proportion of the active substance, namely, the oxides of calcium and magnesium.

Aside from the preceding considerations, we have in most States, two distinct types of limes. In some localities both are available at approximately the same cost; in others there would be a marked difference in price. These limes are known as a *gray* lime, made from a limestone carrying from 85 to 100 per cent. carbonate of calcium, usually with but

little carbonate of magnesium present. The other is known as *white* lime, and is made from dolomite or dolomitic limestones and usually carries about 42 to 44 per cent. carbonate of magnesia and 56 to 58 per cent. carbonate of calcium; that is to say, a molecule of each carbonate go into chemical union with each other.

To test the relative value for the sand-brick reaction of these well marked commercial varieties of lime, the following tests were undertaken:

TABLE XII.

Data:—Molding Pressure, 15000 pounds per square inch.
Steam Pressure, 150 pounds per square inch.
Temperature in Hardening Cylinder, 185°C.
Time Exposed to Steam, 4 to 14 hours.

Number of Test.	Composition of Mixtures.				When Tested.				
			Per Cent. Quicklime.		At once after Hardening.		After Freezing.		
	Parts Coarse Sand.	Parts Fine Sand (Including Impurities.)	Parts CaO.	Dolomitic	Crushing Strength.	Tensile Strength.	Crushing Strength.	Tensile Strength.	Per Cent. Water Absorption.
A*	2	1	10	....	7745	437	9007	371	8.62
B†	2	1	....	10	5187	286	5853	314	9.11

*A is the average of tests number 106, 107, 108, 109, 110 and 111.
†B is the average of tests number 112, 113 114, 115, 116 and 117.

Twelve blocks were tested in A, and an equal number in B, all made in exactly the same manner, with the exception that in A a high-calcium lime was used, and in B, a white or magnesian lime was used.

The differences shown in Table XII are very marked, the use of dolomite lime resulting in a loss in strength, both crushing and tensile, of more than one-third. Another noticeable fact is that the water absorption is greater in B than in A. Why the dolomite limes give a weaker brick is still an unsolved problem. Since MgO is at least equally active as CaO in attacking SiO_2, we can only infer that the magnesium silicate formed is a much weaker bond than the calcium silicate. This is also supported by the fact that there is also more combined water in brick made from sand and dolomite

lime than there is in those made from sand and pure lime.

C—PREPARATION OF RAW MATERIALS.

Now that we have a general idea of the requisites for satisfactory raw materials, the next step will be to determine what preparation they will need.

Beginning again with the sand, if our source of supply is a soft sand-rock, it will need to be crushed and the individual sand particles separated from each other. The machinery best adapted to this purpose will depend, to some extent, upon the nature of the rock to be crushed. If we have to deal with a sand obtained by dredging, it will usually be quite wet and must be at least partially dried, since a large amount of water is undesirable in the mixture. The degree of drying necessary will be dependent on the subsequent treatment prior to pressing.

On account of the presence of too much clay, or of soluble salts from sea water, as would probably be the case with sea-shore sand, it will be necessary to roughly wash the sand. In the first case the clay is floated off, and in the second case the salts are again taken into solution and in that way removed. The arrangements for accomplishing this will depend almost entirely on local conditions.

In any case, if the sand does not contain some very fine quartz, it will be necessary to pulverize a small portion of it. For this purpose a tube or ball mill can be used since they produce the greatest fineness. The Griffin mill will probably be found to be the one most satisfactory for this purpose. However, it will not be necessary to resort to any of this preliminary fine grinding in many cases.

In foreign countries it has been claimed by a few, to be advantageous to roast the sand. The advocates of this procedure claim that chemical combination is rendered more rapid and complete by giving the sand a preliminary roasting. I doubt if the activity of the sand is increased sufficiently to justify this additional expense. The exact value of roasting the sand remains yet to be determined.

Assuming that we have a comparatively pure lime, preferably a high calcium lime, properly burned, it must be hydrated, or in popular terms, it must be "slaked" either be-

fore adding the sand, or in connection with its incorporation into the sand. Owing to the slow slaking properties of magnesian limes, they could not be safely used unless they had been completely slaked prior to the addition of the sand. In the slaking of the lime, and in its incorporation into the sand-mix, lies the main difference between the various patented processes or systems in use. The essential feature of each system is generally the use of some special piece of machinery, or some special manipulation, for this purpose.

The slaking of lime is in one sense a very simple process, consisting in the addition of water to calcium oxide, or calcium and magnesium oxides, which takes the water into combination with it in certain proportions. One would hardly suppose that so simple and well known an operation should form the ground for the issuance of a large number of patents. Such is the case, however, both in this and in foreign countries. This is probably due to the fact that a chemical reaction is involved, and in many cases a reaction will not complete itself except under certain conditions. This is in a large measure true with the slaking of lime. Too much or too little water will yield an inferior product.

Most of the patents, however, are for methods or machines which utilize the heat generated in hydration, to dry out any excess of moisture and leave a product which is easily handled and stored without loss to its chemical activity.

While there are a large number of lime-slaking processes, which differ from each other in detail of manipulation, there are in reality only two distinct procedures; viz.,

1. The time honored method of slaking to a putty with a slight excess of water. This is used in the putty state, or after drying and grinding.

2. The other which slakes to a dry powder.

This is accomplished by adding such a quantity of water as will hydrate the lime but not so much as will leave the hydroxide wet. The excess must be so small that the heat generated by the hydrating of the oxides will expell it. The resultant product usually contains less water than that called for by the theoretical calcium hydroxide, yet there seems to

be no heating nor expansion on the subsequent addition of water for the purpose of using it in the arts or industries.

The method of preparing the lime will, in the nature of the case, govern the subsequent handling of the sand to a considerable degree, since in one case we have to deal with a plastic, tough, sticky mass, and in the other with a dry powder. However, the method of slaking should depend upon existing conditions, and that method selected which will best fit other parts of the process which have been decided upon for good reasons. In order to make the meaning clear a specific case or two will be cited.

Case 1. Wet Sand. If it was quite wet, we would dry some of it and add the unslaked lime to the balance, provided we had a high-calcium lime to work with. The moisture would then be corrected by adding dry sand and lime, or water, as the case might require.

Case 2. Moist Sand. Slake lime to a putty and incorporate. This has its drawbacks on account of the extreme difficulty of getting a small amount of tough sticky matter distributed evenly through a mass of crystals of quartz. I think it has one advantage, though I am not yet able to prove it, viz, that it will probably require less pressure in the machine to develop the maximum strength in the product, than is required where the material is mixed dry. I am inclined to believe the increased cost of mixing would more than cover the expense of drying the sand. If the lime is to be used in the putty state, it will always be found advantageous to work up the putty with all the water that is to be added to the mixture, thus getting it in a slurry or slip form, and in that way to facilitate distribution. But if there is much water in the sand, the amount left to be added to the lime is so small that it is of very little assistance.

Case 3. Dry Sand. This is the easiest to work, since the dry sand and dry hydrate, or the dry ground quick lime, can be readily mixed to a fairly homogeneous mass and the water then added and mixed in. The water will distribute itself to a considerable extent, if after the mixing the whole is allowed to stand in a bin or pile for a short time.

The facility with which a uniform mixture would be

produced from the dry ingredients led us to adopt the third way as the means of preparation for all the materials used in our experimental work.

II—BEHAVIOR OF THE MIXTURE IN THE PRESS.

In the work done to determine what requirements a good brick press for this industry would have to fulfill, material prepared according to the third method, was used. The results obtained will therefore apply in the strictest sense only to that class of material. However, it is the opinion of the writer that any press which is satisfactory for this plan, will answer all the requirements for any of the others. It is the popular belief that the harder a brick is squeezed the harder it would be. But there is a limit at which the increase in strength in the brick would not justify the additional cost of construction and operation of the machine. In order to get some idea of this property of our material, we tried making a block on a hand power screw-press such as is used for making encaustic tiles, by giving it a number of pressures in succession. This block, after hardening, was crushed and compared with a duplicate made with one pressure only. This we found gave us a very decided increase in strength. This showed that we were not getting sufficient pressure, and since we were not able to control our pressure accurately, we abandoned the screw-press and adopted in its place an ideal brick press. This was a Tinius Olsen automatic testing machine, of 100,000 pounds capacity. On this machine we had the conditions of pressure, speed etc. under accurate measurement and control.

From the moment of inertia of the fly wheel, and the pitch of the screw on our hand tile-press, we figured roughly that we were getting from 5000 to 7000 pounds per square inch pressure. We therefore took 5000 pounds per square inch as a starting point, and made a series of blocks, using 5 per cent of each type of lime and the same sand mixtures, using pressures of 5,000, 10,000, 15,000 and 20,000 pounds to the square inch. All were hardened, at 150 pound steam pressure for ten hours.

The results of this work are plotted on Plate I. The

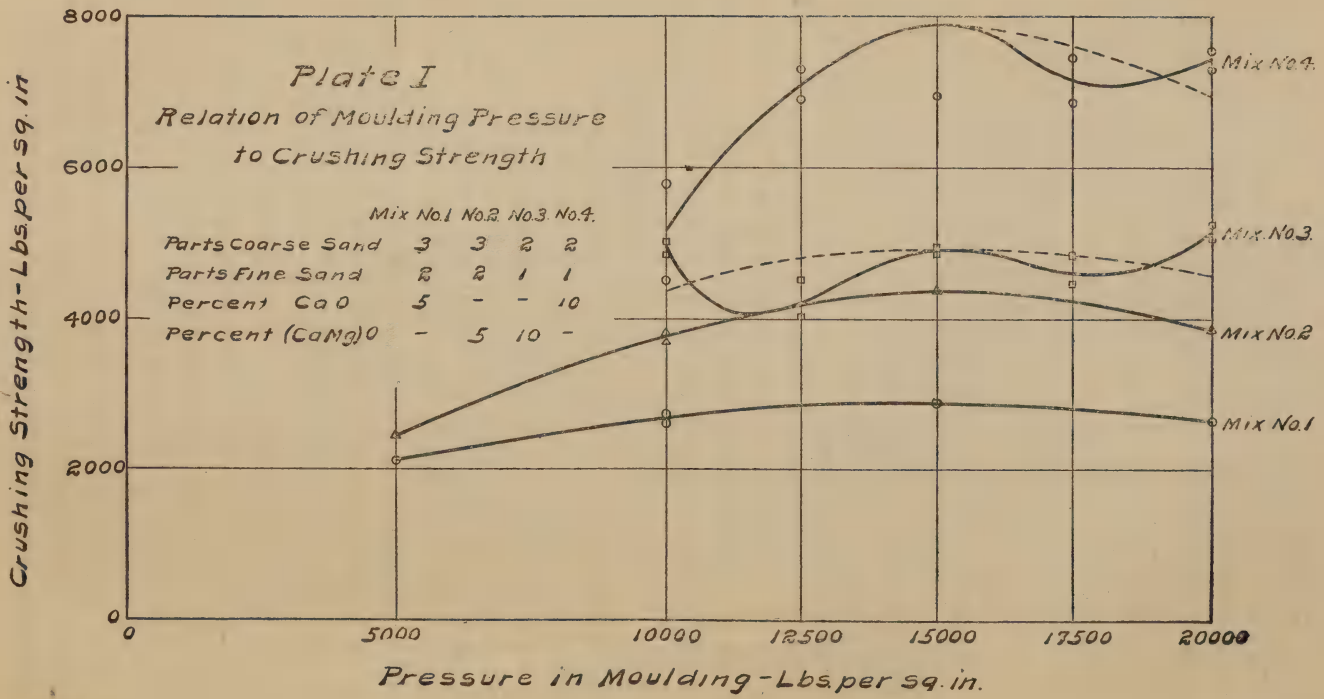


Plate I
Relation of Moulding Pressure to Crushing Strength
Mix No.1 No.2 No.3 No.4.
Parts Coarse Sand 3 3 2 2
Parts Fine Sand 2 2 1 1
Percent CaO 5 - - 10
Percent (CaMg)O - 5 10 -
Crushing Strength - Lbs. per sq. in.
Pressure in Moulding - Lbs. per sq. in.
8000
6000
4000
2000
0
5000
10000
12500
15000
17500
20000
Mix No.4.
Mix No.3.
Mix No.2
Mix No.1

load at which the test-blocks crushed is shown on the ordinates and the pressure used in manufacturing on the abscissae. All represented in pounds per square inch. The two lower curves are the ones that illustrate this group. In both cases, the highest crushing strength is obtained at a die-pressure of about 15,000 pounds per square inch, with a slight falling off at 20,000 pounds.

Realizing the importance of this determination, it was though best to duplicate it, especially as the intervals were 5,000 pounds to the square inch. Although the curves seemed regular and pointed closely to 15,000 pounds as the maximum, it was thought that the correct pressure might be on one side or the other of that figure. A new set of test blocks were therefore prepared dividing the intervals. It was evident from the first curves that it was not necessary to go below 10,000 pounds to the square inch.

This set, as shown in the upper curves of plate I, began at 10,000 pounds die pressure, and increased by intervals of 2,500 pounds up to 20,000 per square inch. Ten per cent of a high-calcium lime was used in one set, and 10 per cent. magnesian lime in the other. The upper curve is the high-calcium lime and the second curve the magnesian lime. Duplicate cubes of each kind were made at each pressure.

Here again in the upper curve the highest point is over 15,000 pounds pressure. The figures are just a little lower for 20,000 pounds, and a marked depression occurs at 17,500 pounds. The second curve is a very irregular one, with 10,000 and 15,000 on a straight line, and 20,000 a trifle stronger, with depressions at 12,500 and at 17,500. Making a smooth curve, as indicated in both by a dotted line, taking 15,000 pounds as a high point, and averaging through, we get curves almost parallel with the two lower curves.

I should like very much to see a more extensive test made on this point, reducing the intervals of pressure to 1000 pounds per square inch, or less. However, I think we have sufficient evidence before us to say that the best pressure is close to 15,000 pounds to the square inch. It required about 75 pounds per square inch of surface exposed to the sides of the molds, to start a brick out of the mold,

when a pressure of 15,000 pounds per square inch had been given. The mold was made of cast-iron only. The pressure required to discharge the brick will be much less when the linings to the molds are made of hardened steel. This reduction in the friction will also slightly lower the pressure necessary in pressing. When lower pressures are used, the upper and lower portions of the brick are denser than the center. This difference is sufficient to be readily observed when using soft molds.

There is a good suggestion in this work for the dry-press brick-machine manufacturers. I should like to see some of them take up this point with reference to dry-press clay products.

The next consideration was the behavior of the loose powder of the mold. The same mixtures were used as in the proceding case, namely 2 parts of coarse and 1 part of fine sand, with 10 per cent high-calcium lime added in one case and 10 per cent. dolomitic lime in the other.

The curves in Plates II and III show the facts as taken from the Olsen autographic plate. Measurements were also made of total compressions, and length after pressure was removed. These were almost identical with that shown in the curves in both cases at the various pressures, 5,000, 10,000, 15,000 and 20,000 pounds. The elasticity or expansion shown was greatest at 15,000 and 17,500 pounds, and least at 20,000 pounds. The difference was only from 0.01 to 0.02 of an inch.

The curves cannot show the recoil at any pressure, except the maximum, but do show the rate of compression for any pressure. The longest curve on upper plate was evidently due to not getting quite so much material in the mold, since it compressed beyond the point it should have done, giving a curve parallel to its duplicate. From the curves in Plate II, high calcium lime and Plate III, magnesian lime, it is evident the behavior is almost identical in both cases. Compression to 61.3 per cent. is accomplished with practically no load, and from that point the load increases very rapidly with each shortening of the block. The compression is less than 0.01 of an inch per inch

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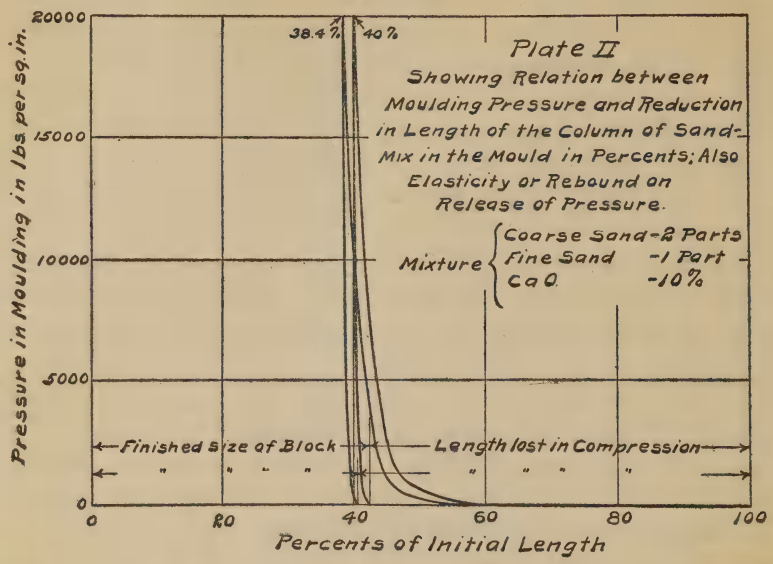


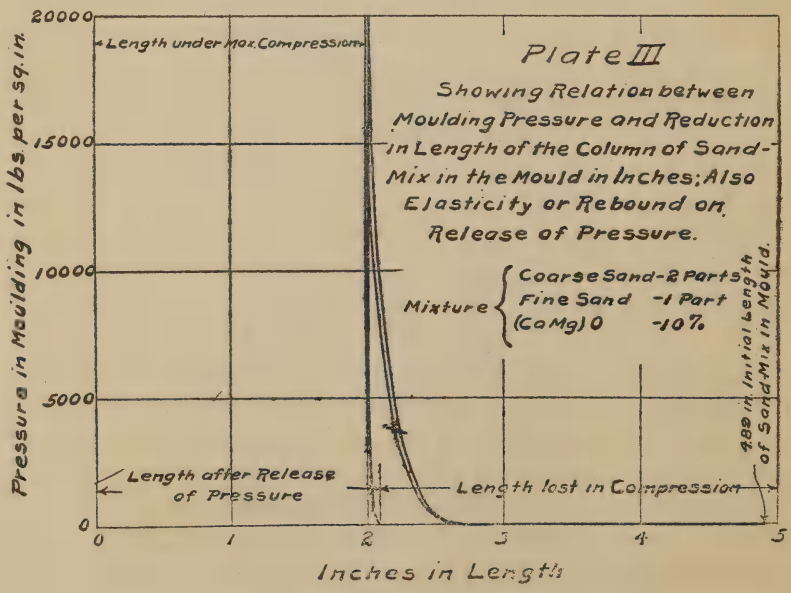


Plate III
Showing Relation between Moulding Pressure and Reduction in Length of the Column of Sand-Mix in the Mould in Inches; Also Elasticity or Rebound on Release of Pressure.
Mixture { Coarse Sand-2 Parts; Fine Sand -1 Part; (CaMg)O -10%
Length under Max. Compression
Length after Release of Pressure
Length lost in Compression
4.89 in. Initial Length of Sand-Mix in Mould.
Pressure in Moulding in lbs. per sq. in.
Inches in Length
20000
15000
10000
5000
0
0
1
2
3
4
5

of length for an increase of 10,000 pounds, or from 5,000 to 15,000. The total compression was 40.9 per cent at 20,000 pounds, springing back to 42.9 per cent as final size.

For different mixtures of sand, the compression will undoubtedly be somewhat different, but will probably follow nearly the same curve, taking the load very rapidly after a pressure of 2,500 to 3,000 pounds is reached.

III—HARDENING.

In this connection I wish to urge on all prospective builders of plants, the necessity of careful and safe construction of the device for holding the head on the hardening kettle. Where accidents have occurred, it has usually been due to some defect at this point. The manner of fastening the bolts to the boiler should be carefully looked into, and no chances taken, since loss of life and destruction of property is sure to follow any carelessness in this direction.

It was known that good strong brick could be made in ten hours steam at 150 pounds pressure. It was not known how much less steam pressure would do, nor was the influence of the time factor known, and whether an extension of time would enable a material lowering of the steam pressure needed. To get data on these various points, the following tests were made as shown in table XIII. The pressures used in making the blocks were 15,000 pounds per square inch throughout.

(See Page 192.)

This table shows that 4 hours time at 150 pounds steam pressure is sufficient; that 6 to 8 hours are required at 120 pounds; that 8 to 12 hours are required at 100 pounds. The samples which contained 10 per cent of feldspar showed marked increase in strength in each case where the time was longest. I note this fact, since it suggests that long exposure to steam probably finally breaks up the feldspar, and in case it did so, might produce efflorescence. Knowing this fact, it would probably be desirable not to hold material containing much feldspar in the kettle any longer than necessary.

I should say general practice is to use 120 pounds steam

TABLE XIII.

Steam Pressure, 150 Pounds.

Hours in Steam.	A		B		C		D		E	
	Crushing Strength.	Tensile Strength.	Crushing Strength.	Tensile Strength.	Crushing Strength.	Tensile Strength.	Crushing Strength.	Tensile Strength.	Crushing Strength.	Tensile Strength.
4	7896	544	5303	392	5282	591	4514	470	4441	330
6	7994	390	5045	199	....	....	....	....	....	...
8	7404	509	4957	262	6170	632	4249	430	4491	337
10	7767	464	4902	284	...	....	....	....	....	....
12	7514	337	5064	250	6165	556	4543	434	4924	349
14	7894	380	5849	329	....	....	....	....	....	....

Steam Pressure, 120 Pounds.

4	6989	....	5989	....	5403	....	4300	....	5760	....
6	7063	....	6495	....	....	.. .	....	....	...	....
8	8545	....	6038	....	5868	....	5142	.. .	6718	....

Steam Pressure, 100 Pounds.

4	6385	....	5921	....	4280	....	4048	....	4588	....
8	7566	....	6507	....	5564	....	4456	....	6544	...
12	7494	....	5753	....	....	....	....	....	....	....

pressure, and keep it on 8 to 10 hours, and in my opinion that is good practice. It usually takes about one hour to get the pressure up, and another to blow off and cool down sufficiently to be handled. The time required to raise the temperature will depend of course on the steam producing capacity, and the size of the inlet pipe, and the blowing off time depends on the size of the outlet pipe, etc. If the pipes are large enough and the boiler capacity is available, the temperature can safely be brought up very rapidly. I have put green brick in at a temperature of 130° C., and in about five minutes put on the steam, bringing it up to 150 pounds pressure in ten minutes more without any apparent injury to the brick. The brick on which I was working only carried 5 per cent moisture, however, and were small, viz 2 inch cubes.

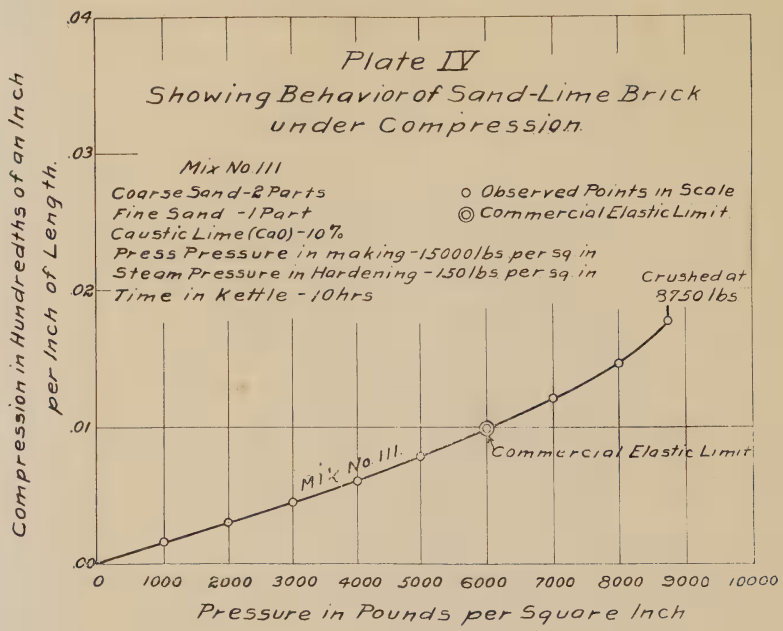
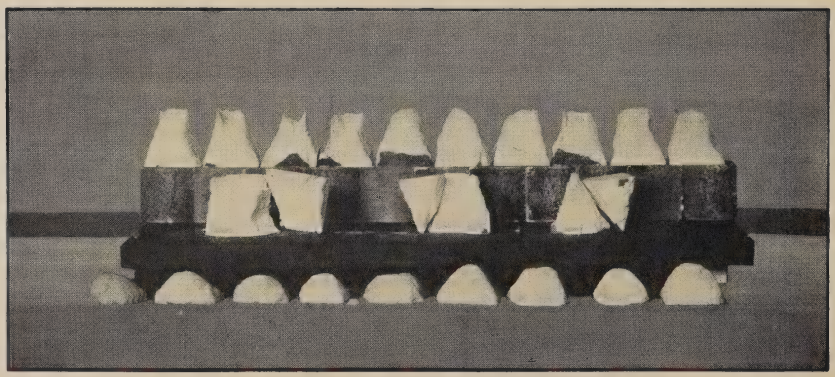


PLATE V.



CUBES OF SAND-LIME BRICK, SHOWING THE SHARP ANGULAR FRACTURE AFTER CRUSHING. IN THE LOWER ROW ARE CUBES OF COMMON MORTAR, SHOWING ROUNDED GRANULAR FRACTURE.

IV—TESTING.

By Chemical Methods.

The testing was in the main mechanical. However, the soluble silicic acid was determined in a number of cases, and enough results were obtained to show how much dependance could be placed in this determination as an indication of strength. It is merely a measure of the amount of bonding material.

By Mechanical Methods.

The mechanical test is always best, whenever it is feasible to make it. The results appeal more strongly to the public, even if the other were equally accurate, which is probably not the case, since the physical structure of the mixture has a decided influence on the strength, regardless of the amount of bonding material.

An autographic automatic Tinius Olsen testing machine, driven by power, was used for all tests. The autograph was only used on *types* of material, since more satisfactory and rapid work could be done without the autograph attachment on the machine. A ball and socket was used, as well as pasteboard to take up any uneveness of the block, on all except those on which curves were taken.

The crushing and tensile strength were determined in each test. Two to three blocks were crushed in most cases and the average reported. For the tensile strength, when two were pulled the average is given. Every brick made was tested, so that the results represent all the data obtained, not merely the best that it was possible to pick out on a single piece out of a dozen. Plate V shows a number of sand-brick cubes as they appear after crushing. The sharp angular cones and the splintery fracture show clearly that the material crushes exactly as a hard rock does. For comparison, a row of cubes made from lime mortars, which have been allowed to set and dry, are shown. The rounded outlines and low cones show beautifully the wide difference in structure and strength, though both sets of cubes are made of lime and sand.

A few of the brick made were set away in a dry room,

to try the effect of age upon them. These were duplicates of brick which had been tested, so that by comparison we could find out if there was any material change. There was not any marked change in strength, after forty days exposure to dry air, except in the specimen carrying 20 per cent kaolin. This showed considerable weakness. However, had these brick been moistened from time to time, they would have shown increased strength. This is due to the fact that CO_2 acts very slowly, if at all, on dry $Ca(OH)_2$. We should not place any importance on the above test unless it were carried out through several years, at least.

Resistance to Frost.

This test was made very severe. Duplicates of blocks which had been tested were used. These duplicates were made at the same time as the brick which were considered the standard, to enable us to see if weakness developed. About two weeks elapsed after hardening, before they were frozen.

The test was carried out in the following manner:— The lot of blocks to be tested were weighed; then dried at 110°C; weighed again; then soaked for 48 hours in water; then weighed; and the water absorbed figured as per cent of the dry weight. They were then placed, while still saturated with water, in a rack composed of wire netting and lowered into an empty ice-can, which was immersed almost its entire depth in the freezing brine at an ice plant. The temperature of the brine ranged from 12° to 15° F. The bricks were frozen to the centre in less than four hours, but were never taken out under that time. In this fully-frozen condition, they were lifted out, rack and all, and dropped at once into another can containing water at a temperature of 95° to 105°F, and thawed out entirely. The interval needed was less than two hours, but that time was always allowed. From here they were lifted dripping wet and dropped at once into the freezing temperature. This was repeated 21 times on all blocks tested.

As an experiment three cubes were put into the distilled water, which was then frozen solid. The ice was then

thawed and refrozen several times. The cubes showed no signs of breaking down. These were not tested.

The material after this severe treatment was further abused, by being dried out in a few days at a temperature of 125°C, after which it was tested. Many results have been given in the preceding tables in such a way as to be comparable with unfrozen material, and the facts have been, in a measure, brought out prior to this statement.

The blocks, almost without exception, as may be seen by going over the tables, showed marked increase in crushing strength, and in some cases increase in tensile strength as well. Usually the tensile strength was slightly less, if any material change had taken place. However, duplicates on the frozen material were not available in every case, and the results are not so conclusive on this account.

The reason of this increase of strength must be due to one of two causes:

1. The lime was not all combined with silica, and this uncombined lime took up carbonic acid from the water in which they were thawed out. This is very likely for two reasons. First, the water was drawn from a deep well near Columbus, Ohio, and I know from previous experience that these waters are rich with calcium and magnesium salts and also carry much carbonic acid in solution. Second, those specimens which were highest in lime showed greatest increase in strength after freezing.

2. In case the calcium hydro-silicate formed has hydraulic properties, which I doubt, those properties would be developed by constant soaking in water and would naturally develop more strength. I think, however, if the strengthening action were of a hydraulic nature, it would be most marked on the tensile strength rather than the reverse.

Resistance to Fire.

In order to determine the properties of sand-brick under fire, the following experiment was carried out.

Five blocks, representing five different sand-brick compositions were placed in a muffle kiln and the temperature brought up rapidly until Seger cone 6 was down. This cor-

responds roughly to 1250°C or 2282°F. Eight or ten hours was required to get this temperature. The blocks were taken out while still warm. All the blocks were perfect. The only change observable was that they were whiter, and had taken on a semi-vitreous lustre. There was neither fire-shrinkage or expansion. The blocks when cool were exactly the same size as when put in. Ten per cent of lime was used in each case, and both high-calcium and magnesian limes were represented, as well as ten per cent kaolin and ten per cent feldspar mixtures.

Not satisfied with this, the muffle was brought to a white heat, and five more blocks representing the five mixtures were put in on top of the muffle, and the heat continued to cone 6 or 8. These samples had but 5 per cent of lime in them. Before the opening to the kiln was entirely closed, all the blocks which had either clay or feldspar in them exploded. Those composed of pure quartz-sand and pure or magnesian lime, stood the test all right. They again showed the only change in greater whiteness and more porosity due to loss of combined water. They were not so hard as the first set, since with only 5 per cent lime the point at which the amorphous silicate would form was not reached. This shows clearly that brick made from comparatively pure quartz sands will stand a very high heat without injury, since even if the small amount of calcium silicate present were made fluid by heat, there would be no deformation, unless there was great pressure on them. The mass of sand particles built up and wedged in place would not require much to hold them in relatively the same position.

Nothing was done to determine the expansion while hot, but with low lime content it would not be far from that of pure quartz, and about the same as silica brick. Dr. E. Cramer states that a sand brick tested, the composition of which is not given, melted to a white glassy mass at Seger Cone 33, and that in a porcelain kiln, another specimen gave a linear expansion at cone 17 of 2.08 per cent. Further heating at same temperature gave an expansion of 2.72 per cent.

The figures quoted above were given in the last Convention of the Lime, Sand Brick Society, at Berlin, Germany.*

Since these brick are 90 to 95 per cent. silica or quartz, the heat conductivity must be very low, since quartz it is a much poorer conductor of heat than glass. Flint glass has a coefficient of heat conductivity 0.143 while that of quartz sand is only 0.0131.

Electrical Resistance.

For electrical resistance, 8 plates were tested. They were made 4x4x½ inches with a half spherical indentation in the center leaving a thickness approximately one-fourth inch in the center, where the electric terminals were applied. The rupture invariably occurred from ⅛ to $\frac{1}{16}$ of an inch from a line joining the two terminals of the instrument, showing that the current arced through the hydrous silicate bond, as would be expected. The voltage required to puncture the one-fourth inch thickness varied from 15,000 to 20,000 volts.

Comparative Properties with Other Materials.

With comparatively pure sands, the brick are white to grayish, depending on the sand. Small amounts of oxide of iron do not materially affect the color. The bricks may be colored red, black, yellow, brown or green, and these colors are not or subject to wide variations, *i. e.* by duplicating the mixtures, the resultant colors will be duplicated. In ordinary manufacture, there is great uniformity in color.

The brick are very slightly hygroscopic. The average of 20 determinations show that about 1½ per cent of water is retained in the normal air-dried sand-brick. The hygroscopic property is strongest when clay is present.

The water absorption is almost complete in 24 hours; in 48 hours the brick made by us took up from 8 to 10 per cent of water, calculated on the dry weight of the brick. The majority of the results were close to 8 per cent, as may be seen in the tables previously given.

*Thon-Industrie Zeitung, No. 31, 1903.

The following table gives a comparison of strengths shown by sandstone used for construction, and of sand brick.

TABLE XIV.

	Natural Sandstone.	Sand-Brick.
Weight per cubic foot.....	137 lbs[1]	136 lbs
Absorption.....	7.3%[2]	8%
Crushing Strength.....	6535 lbs[3]	7745 lbs[5]
Coefficient of Elasticity.....	165440[4]	600000[6]

1. Average of 16 samples, Bulletin Wis. Survey, No. IV, p. 402.
2. Average of 16 samples, Bulletin Wis. Survey, No. IV, p. 402.
3. Average of 51 samples, Bulletin Wis. Survey, No. IV, pp. 393-394
4. Average of 28 samples, Bulletin Wis. Survey, No. IV, p. 399.
5. Average of 12 samples tested by us.
6. Calculated from Curve No. 111 on Plate IV.

As you will note, the weight and absorption are very close. The crushing strength is in favor of sand brick as well as the elasticity. While the average strength of a large number of sandstones is less than that of sand brick, there are some sandstones of great strength, as is shown from the following record taken from "Brown-stones of Pennsylvania." A stone from White Haven, Pa., Appendix, 30, gave a crushing strength of 29,252 pounds per square inch.

The coefficient or rather modulus of elasticity is an arbitrary figure supposed to represent the theoretical load at which an inch cube would be pressed to zero length, if the block were perfectly elastic to that point. This figure is obtained from the amount or rate of compression, or shrinkage in length with increment of load, up to the commercial elastic limit, and the load at the elastic limit.

The commercial elastic limit is that point at which the compression curve increases by 50 per cent or more. An example will make this more clear. We will assume that with a load of 5000 pounds on a one inch cube, the shrinkage in length would be 0.01 inch; that is 0.002 inch for each 1000 pounds of load. Now, if when another 1000 pounds is added to the 5000 already on, the total additional shrinkage is 0.002 and 0.001 inches, or 0.003 inches, the commercial elastic limit would be 5000 pounds per square inch. The

high modulus of elasticity shown by sand brick means, of course, that they will make a very rigid structure.

This property of sand brick is perhaps made more clear by the statement that a sand brick cube with a load of 1000 pounds per square inch, only shrinks 0.00125 inch in length. Now since only 250 pounds per square inch is allowed to be placed on the best Portland cement mortar by municipalities, the greatest load that we could ask the brick to carry would only cause a compression of one forth that given, or 0.00041 inch per inch of height. This means that in any building, bridge or other structure which is called upon to carry a varying load, there will be little or no deformation due to this load. In other words very rigid structures may be made from this material.

The highest modulus of elasticity quoted in bulletin of Wisconsin Survey, No. IV, p. 399, is one from Alblemans and is 400,800. Limestones go sometimes as high as 1,800,000, and some granites above 2,000,000.

V—MECHANICAL EQUIPMENT.

The mechanical equipment of a plant consists of:—

(1) Power and transmission.
(2) Lime preparing machinery.
(3) Mixing apparatus.
(4) Presses.
(5) Hardening cylinders.
(6) Conveyors.
(7) Tracks and trucks.

Taking these up in order:

(1) Power and transmission will not differ materially from that in other industries.

(2) Lime-preparing machinery properly belongs to the lime industry, since if a hydrated lime is used it will probably be just as well to buy from the manufacturer, unless the lime is burned on the place, since the sooner the lime is hydrated after burning, the better will be the product. Those interested in this subject will find it discussed in the bulletin on the Lime Industry of Ohio, issued by the Ohio Geological Survey, in 1903. When quick lime is used, it

will be necessary to grind the lime, if bought in lump form. For this purpose either Stedman or Sturtevant mills may be used; either should be preceded by a small crusher.

Mixing Apparatus.

(3) A machine which might be mentioned in this connection, although it is not strictly a lime-preparing machine, is that A. G. Schwarz, of Zurich, Switzerland, in which the machine is heated by steam pipes, and the hydrate is dried by producing a vacuum. The excess of water is pumped out as vapor.* This machine is also used in the quick-lime process of manufacture, as a total preparing machine.

Other machines for mixing in either process are edge runners, wet and dry pans, and various mixing machines of the pug-mill type. I think the latter is the predominating type of machine in use. Any of the above named machines are efficient, if the mixing is continued long enough. Considerations of economy in power, durability of machines, available space, etc., should therefore decide on the proper machine for any particular case.

The Schwarz machine offers a means of always maintaining the moisture constantly the same in the brick before going to the press. When using other machines, the workmen soon acquire great skill in judging the correct moisture condition of the mix, so that with care there is but little trouble from this source.

Presses.

I think I am safe in saying there is no press made today which fulfills all the requirements of sand-brick industry. I do not wish to be understood as saying there are no American or European presses which will make good brick, because there are a number of them made on both continents. If we could combine the good points of each, and improve a few minor defects, we would have a very good press. The requirements which a good press must fulfill are these:

1st. The press must be able to regularly deliver a pres-

*"Silico—Calcareous Sandstones"—Ernst Stoffler.
See Also Engineering News, February 19, 1903.

sure of from 200 to 250 tons per each brick, and yet not break down if by accident the pressure rises somewhat higher.

2nd. The filling of the mold must be accomplished with great accuracy and uniformity.

3rd. All working parts must be so arranged that they will be free from contact with loose sand; otherwise, they will cut out at an alarming rate.

4th. The dies, and mold linings, must be made of the hardest material obtainable.

That a pressure of 200 to 250 tons per brick is essential to the development of good strength, was clearly shown in the discussion of the behavior of the mixture in the mold. Statements and results previously given also show that there is necessity for a press to stand much more than the normal load, since the strain on a press increases at a tremendous rate, with a slight increase in the amount of the mixture introduced, or any increase in its volume and weight such as might be brought about by some accident in the preparation of the mixture. The above also accounts for the necessity of accuracy in filling the molds. The lack of plasticity in sand, and its resistance to flow and adjustment of shape under pressure, is evident to all. Therefore, even distribution of the loose powder in the mold is essential.

The above refers to presses driven by direct gearing, in which the stroke of the plungers is fixed, and the pressure therefore directly dependent on the amount of material in the mold. This is the general type of machine in use. If the above requirements are not met, you can expect many break-downs in this type of machine. If, however, a press were constructed that put on a certain desired load and no more, or one which had a fixed stroke but also had some means of releasing the strain when it reached the danger limit, the result would be an occasional large brick perhaps, instead of an occasional broken press, with its consequent annoyances, expense and loss of time.

The third requirement is self-explanatory and evident to all.

The fourth is necessary to the reduction of friction and

more even distribution of pressure, as well as to save the annoyance and loss consequent to frequent changing of the mold linings.

The increase of press pressure increases the friction and abrasion of the mold linings and dies. It was found necessary when working with cast-iron molds, to raise the molds clear from the bed plate, so that the brick rested on the bottom die, so as to get pressure from both top and bottom. It is therefore likely that for the best results the pressure must come from both top and bottom.

It is probable that the friction on the sides of the mold, and the resistance to flow of particles will limit the thickness of a block which can be manufactured satisfactorily to four or five inches. Possibly a press may be so made that one charge may be added and given a definite pressure, and then another added and pressed on top of it; in this way, large blocks might be built up. The limiting factor here would be ability to push the block out of the mold without destroying it. Blocks made in this way would be expensive of course. I think the limit in thickness might be increased when necessary, by increasing the lime and moisture content. These would both tend to reduce friction, and increase movement of particle on particle, but at the same time increase the cost of production.

On account of the resistance of this non-plastic mass to flow, or the movement of particle on particle, it would be well that a press should not at once release the pressure given; or it might be better still to repeat the pressure. It seems that the hydraulic press might have some advantages, if adapted to this industry.

Considering the presses in use in this country, we can truly say they all have their merits, and if we were able to combine the good points of all in one machine, we would have a fairly satisfactory one. They all have their faults, however. One fault is common to all; they are not built to give the very high pressure which has been shown to be necessary. Since strength is developed in the brick either by giving it high pressure in the press, or by increase of the lime content, it follows that brick of equal strength can be

made with much less lime, if the press pressure is high enough, and it is probably cheaper to give this pressure, than to use larger amounts of lime.

Aside from this common fault, each press has its own weak points. Taking the Kahl press, which is a German press, soon to be manufactured with some improvements by the Ohlemacher Brick Company, of Michigan City, Indiana, we have a machine built to stand 150 tons per brick, and one which seems to do very good work up to about 100 tons, or a little more perhaps. This machine is built broad and low with the wearing parts well protected from the sand. The floor space of 1,000 bricks capacity is very large. This is always a disadvantage. The press consists of a rotary table, which first passes the empty mold under a special measuring device, which has the loose material already measured, and which drops the sand when the mold is in the proper position. The table rotates about 135° farther around and the brick gets its pressure from below, this portion of the table now being under a very heavy overhead arm. The table next carries the brick out from under the arm, after which the brick is pushed up flush with the table and may be picked off the head of the die without any scraping, or spalling. The pressure is delivered directly by an eccentric, working under the table. This is a weak point, which is to be remedied in all new machines. This is probably a weak point in any machine called on for enormous pressure. This machine when seen in operation by the writer was giving brick with clean-cut edges and corners, with almost no failures. One size has a capacity of 12,000 to 14,000 per day of ten hours, and the other, 20,000 to 23,000.

The Komnick press, another machine of German type, is used by the American Sandstone Brick Machine Company, of Saginaw, Michigan. It is an upright machine, with a smaller rotating table, and filling device similar to the Kahl press. The method of delivering the pressure is different, being given from above. This machine is supposed to give a pressure of about 100 tons per brick.

The Kahl press only makes one brick at a pressure; the Komnick, makes two. It occupies a little less floor space

than a press of the American type having twice the capacity. It has a capacity of about 10,000 in ten hours.

A weak point in this machine is that some of the wearing parts are not protected from the sand. When seen in operation by the writer it was not giving brick with clean edges. This fault was not inherent in the machine, but was probably due to the setting of the mold linings, and the condition of the die-heads.

This firm intends manufacturing a press of this general type with some improvements, making it double-geared and simplifying it at several points. This is to replace the other press in all their new plants.

Since sand-brick, when first pressed, are so tender that they do not stand pushing around and handling without injury, the rotating table is the one thing characterizing the German press which recommends it, and it was the result of an effort by the German manufacturers to adapt the press to the need of the industry.

The various American dry-press brick machines used in the clay industry are too well known to require any description. So far as known to the writer, they are the only machines of American construction yet applied to the making of sand-lime brick. They have greater strength, greater durability and greater capacity than any other. They have, however, one serious fault. The brick is pushed off the head of the die by the mold charger in such a way that many sand-brick are injured by having corners broken off, or the edges made ragged by little spalls breaking out. Two American brick-press companies think they have solved this problem, and will soon have new machines out. It is to be hoped that their anticipations may be realized. It will not be long, at any rate, until the problem is solved by some American mechanic. The writer favors the use and development of an American press. Even if many defective brick must be thrown back for a time, the American press will make more brick with less expenditure for labor and repairs than any other, and its use will soon lead to the over-coming of its present defects. It must be borne in mind, that it was

not designed for sand-brick at all, and it could not properly be expected to do this work without adjustment to it.

Hardening Cylinders or "Kettles."

(5). Hardening cylinders were described by the writer in a previous paper[1]. The following notes are supplementary to what is there given.

The head should be handled by an overhead crane or a block and tackle. Hinged doors with a wheel on the bottom, and a track for it to run on, have been used. These are clumsy affairs to move and occupy much space, and should never be recommended. The bolts should be so fastened to the kettle, that the head can readily be swung into place. These bolts are usually 1¼ to 1½ inches in diameter.

The size of these hardening kettles varies from five feet six inches to seven feet in diameter, and from 35 to 67 feet in length. They should be constructed of ⅝ inch to ¾ inch iron or steel plate. There has been considerable discussion among the German manufacturers as to the size of kettle which is best. From these discussions, I would infer that the majority are in favor of the larger sizes. The friends of the smaller size put forward the argument that the brick should be put into the cylinder at once, and that with the larger ones they would have to stand twice as long. This is true, but the experience of the writer would indicate that the difference in time of stand, which would be only a few hours between pressing and steam treatment, does not materially hinder the development of the usual strength. When working brick very moist, the danger of damage from standing before steam treatment, is increased, since the more moisture present the more rapidly will the free calcium hydrate take up (CO_2) carbon dioxide.

With the small cylinder, the cost of both labor and fuel will be slightly increased, as has been shown by Thiessen[2].

The size of the kettle which will be best, will depend on 1st, the plan of operation adopted at the plant, and 2nd, on the capacity of the plant, which means the press capacity.

1 Transactions American Ceramic Society, Vol. IV.
2 Thon-Industrie Zeitung, Vol. 26, No. 104.

With a press capacity of 20,000 brick in ten hours, I should recommend working with units of 10,000 brick, and should build each kettle to carry that number. If, however, the press capacity were only 15,000 per ten hours and the plant was to be operated only through the day, it is obvious that kettles of 10,000 capacity would not be convenient or economical. The customary size is six to seven feet in diameter by fifty to sixty feet in length. This size will, in my opinion, be not for from correct in most cases.

Tracks and Trucks.

(7). Of the trucks, nothing need be said except that they should be well made, strong, and easy running. No trucks should be used without ball or roller bearings, so that the power used in moving them will be small. The tracks also should be first-class, laid with rails of good weight and kept in good alignment, to avoid jolts or jars on the brick, especially before hardening.

VI—DISCUSSION OF THE MERITS OF THE VARIOUS SYSTEMS, INCLUDING PATENTS.

Five systems or processes of manufacture have been exploited in this country. Three of these have plants in operation today.

The American Sandstone Brick Machinery Company, of Saginaw, Michigan, are putting in plants after the system used by F. Komnick, in Germany. This company has one plant up. The Ohlemacher Brick Company, of Michigan City, Indiana, represent the Kleber system as patented in the United States. This company has the pioneer plant in the United States.

Mr. H. E. Brown, of Coldwater, Michigan, is exploiting a patent on the use of *dolomite lime*.

The Schwarz System Brick Company, New York, has the Schwarz system to offer.

H. Huennekes & Company, of New York, are exploiting the Huennekes system, which is based on the United States patent of Joseph Prior. This company has three plants in operation today.

Patents on Hardening Processes.

There are quite a number of patents which bear directly or indirectly upon the sand-brick industry as defined by us. There are not many, however, that have real merit. *There is no patent on the process of hardening with steam under pressure in the ordinary way, since Dr. Michaelis, of Germany, the originator of this idea, allowed his patent to expire some years ago, thus giving it to the public.*

However, there have been granted in the United States two patents on hardening processes, which bring about the same reaction and essentially by the same agent—hot steam or steam pressure. While both of the processes will harden the brick, I cannot see where they introduce any advantage or economy over the old way of doing it; in fact, I think there are several factors introduced, which would bring about a loss of heat, in place of economy.

These patents are:

Patent 681580, August 27, 1901, granted to *Carl Rensing*, Berlin, Germany.

Patent 683337, September 24, 1901, granted to *Walter Schulthess*, Zurich, Switzerland.

An electrical hardening process has also been patented.

Patent 661443, November 6, 1900, granted to *Emery Coulon*, Blatson, Belgium.

But the latter, as outlined in the specifications, would probably be too expensive to receive any commercial attention in this country. So far as I have been able to find out, none of these three patent hardening processes have received any commercial impetus.

Patents Covering Objectionable Procedure.

In the United States, there have been granted between January 1, 1892, and September 30, 1902, twelve patents, which bear directly upon the sand-brick industry. Three of these have objectionable features, considered from the point of material produced. Good brick can be made by any of the other nine. The question simply resolves itself into one of economy of manufacture, so far as they are concerned.

Patent 693906, February 25, 1902, granted to *Edward*

Rott, of Cassel, Germay, covers mixtures of clay and lime hardened in steam. The quality of material produced by clay and lime hardened by steam has been discussed earlier in this report, and needs no further comment.

Patent 685094, October 22, 1901, granted to *Sven Edmund Boirie*, of Rognhildsborg, Sweden, makes use of nitric acid, in the mixture. This is almost sure to leave soluble salts in the finished product, which would be very undesirable.

Patent 470333, March 8, 1892, issued to *Charles George*, of Berlin, Germany, gives the brick, after steam hardening, a bath in a solution of calcium-chloride. If he were to forget to give his brick their bath, they would be more desirable.

Patents Covering Impractical Procedure.

While good brick can be made under the next three patents, I do not think they are feasible commercially.

Patent 624900, May 16, 1899, granted to *Thomas Barber*, London, England. I will quote claim No. 1 for this method. "The process of manufacturing artificial stone, which consists first in submitting the materials to a vacuum to exhaust the air therefrom, then submitting them to the action of hot water under pressure, then submitting them to the action of steam under high pressure and removing the water, then again submitting the materials to a vacuum while maintaining them at a suitable temperature till dryness is reach, substantially as described." The brick must stay in the mold during this entire procedure.

Patent 591168, October 5, 1897, granted to *Christian Heingerling*, of Frankfort-on-the-Main, Germany. There are three claims: claim 1 would make good brick, but they would have to remain in the mold while being subjected to vacuum after molding; claim 2 dips the brick in oleagenous substances, which would be objectionable for most purposes; claim 3 hardens by carbonic acid gas.

Patent 707898, August 26, 1902, granted to *Teodor Boas*, of St. Hyacinthe, Canada. This patent covers the use of magnesium-silicates with lime, and steam hardening. There are eight claims. I am not prepared to say what the results would be for the first four of these, but with the bal-

ance, where sand and lime are used with magnesia in excess of the lime, I think a good brick could be made. However, there are not many locations where magnesia or magnesium-silicate can be had cheaper than sand. Since probably the only office of the magnesia compound would be to replace sand, it would do just as well to use cheap sand.

Patents Covering Practical Procedure.

Patent 684649, October 15, 1901, granted to *Wilhelm Olschewskey*, Berlin, Germany. The only new feature introduced in this patent, is the heating of a portion of the sand mixed with lime in a closed vessel. The balance of the sand and water are added later to cool the entire batch. The additional manipulation here, of course, will slightly increase the cost of production. It is necessarily an intermittent process. Since brick are made to answer all requirements without this extra heating and manipulation, this process is not likely to become popular in this country.

Patent 702611, dated June 17, 1902, application filed December 4, 1901, granted to *Oscar Hugo Anderson*, of Stockholm, Sweden, assignor by mesne assignments to the Silicate Brick Syndicate, of Montreal, Canada, a corporation of Delaware. The essential feature in the claims of this patent, is the slaking of lime in dry high-pressure steam *at the same time*, and *in the same hardening cylinder* as the bricks are hardened in. The principle of slaking lime in dry steam is not new, since Walters published the properties of lime prepared or hydrated in dry steam a number of years ago. The novelty of the patent must therefore lay in the slaking at the same time the brick are hardened.

The inventor fails to call attention in his specifications to the most valuable feature of the entire process, namely, the fact that all the heat of the chemical reaction of the water on the lime is utilized. The heat generated is considerable. And all the heat given off by the slaking lime in the hardening cylinder means that just so much steam is saved from condensation by radiation or in raising the temperature of the brick and the trucks up to the temperature of the steam. The passage of the steam through the hardening

cylinder with sufficient rapidity to keep it essentially free from moisture, would be an expensive operation. It is not necessary, however, that this be done, since moist steam will do no harm so long as the temperature is maintained.

The practice recommended in this patent, with the exception that the lime is practically slaked by water before being introduced into the hardening cylinder, is represented in this country by the practice of the American Sandstone Brick Machinery Company, of Saginaw, Michigan.

In April 1900, F. Komnick, of Elbing, Germany, issued a pamphlet "Sandsteinziegel-Industrie," in which he shows a container for slaking lime under high pressure steam, at the same time that the brick are hardened.

At Saginaw, Michigan, there is a very neat little plant, 12,000 to 14,000 in twelve hours, operating after the system of Komnick. This plant has some minor faults in its arrangement, recognized by the owners. These will be corrected in all future plants. The procedure at this plant is essentially as follows:

The lime is prepared by adding water to quicklime in iron boxes of such size as will go under the brick trucks in the hardening cylinders. After the addition of the water, the boxes are allowed to stand a short time and are then placed in the hardening cylinder. Any lime unslaked by the water is fully hydrated by the steam during the hardening of the brick. If, on the other hand, a little too much water is added, the steam drys the hydrated lime. This gives a very satisfactory lime-hydrate to work with. There are always some lumps which do not entirely break down, so the hydrate must be ground before mixing with the sand.

The ground lime-hydrate and sand are shoveled into an elevator, which carries it to the mixing machine. This machine consists of two shafts studded with paddles turning towards each other. The paddles are so set as to gradually carry the mixture to the other end, which feeds into the press. The press used, has been described. Short hardening cylinders (27 feet) are in use here. This is not an essential feature of the system, however. My observation of the material produced, was that the lime was not evenly distrib-

uted. This must be due to one of two causes, *i. e.*, either insufficient grinding of the lime, or insufficient mixing later. Both finer grinding and a second mixing machine would be perhaps desirable.

With almost any other method of preparing the lime, the imperfect distribution of the lime would be dangerous to the product, but with this method of preparation, the only undesirable feature is that the full value of the lime as a bonding material is not obtained. This system of manufacture evidently will not be the cheapest, since the users of quicklime eliminate the cost of the preparation of the lime as indicated above.

Patent 697391, April 8, 1902, granted to *Herman Elisha Brown*, Coldwater, Michigan. This patent covers the use of lime produced from the calcination of dolomite limestone. There are no plants working on this system today, but the contract has been let for the machinery for one to be put up at once at Jackson, Michigan.

As previous statements would indicate, this type of lime must be thoroughly slaked before mixing with the sand, and more time will be necessary for slaking than with hot limes. The mixing machine contemplated in the new plant, is one which has been used in mixing asphalt and sand. Since it is a machine which holds the material until dumped, it should give good results if the mixture is retained until the lime is completely distributed. The hardening cylinder contemplated is extreme in length (76 feet). In my opinion this is a mistake, for any thing except perhaps, a plant of 150,000 to 200,000 brick per day. The back end of such a cylinder will have very bad light. And further, it will be very difficult to keep such a long cylinder from creeping on the foundation.

This process obviously will not be the cheapest one since, as has been previously indicated, slightly more of this lime is needed to produce the same strength as of a hot lime. However, there are no doubt locations where this kind of lime can be had at a sufficiently lower cost to more than over-ballance any *slight* drawbacks which it may have.

Patent 686333, November 12, 1901, granted to *Paul Joseph*

Prior, of Cologne, Germany, assignor to Heinrich Hünnekes, of Straelen, Rhineland, Prussia, Germany. The essential feature of this patent is the introduction into the hardening cylinder of the alkali salts, potassium and sodium carbonates, in such a way that the steam introduced shall pass over the surface of the salts, claiming that in this way potash and soda are introduced into the brick. This patent has been exploited in this country and is better known under the name of the "Huennekes System."

The properties of potassium and sodium carbonates, are such that it is difficult to see how they can be carried up and into the bricks to any extent by the steam. After seeing a plant at Pittsburgh, Pennsylvania, which operated according to this system, the writer concluded that the alkali salts were dissolved and carried out by the water which is inevitably condensed in hardening the brick by steam. This being the case, the alkali salts could do neither harm nor good, so long as the steam inlet and the salts were kept under the trucks which carry the brick. If, however, the alkali salts were suspended over the brick, and the steam then blown over the salt containers, there might be positive harm done by the mechanical action of the steam, splashing the solution of potassium and sodium carbonates over the surface of the brick. These salts would later be apt to show up as a white scum on the brick.

Owing to the fact that three plants were working in this country under protection of this patent, and that the promoters of this system were making rather strong claims as to the desirability and advantanges of this system over all others, it was deemed advisable to make an investigation of the advantages, if any, to be derived from the use of potash and soda.

Accordingly, a mixture of four parts of the coarse sand used in earlier work, and one part of fine-ground flint, and ten per cent. high-calcium lime was made up, and three cubes and three brickettes made from it with a press pressure of 15,000 pounds per square inch. These were hardened in a hardening cylinder, in which the steam inlet deliv-

ered the steam over the surface of potassium and sodium carbonates exposed in shallow pans. This was accomplished by closing the end of the steam delivery pipe which was laid on top of the shallow pans. This pipe had a large number of holes on both sides of it so that the steam came out all over the surface of the salts. The cylinder was heated above 100°C before putting in the bricks and the alkali salts, so as to have as little condensation as possible, but nevertheless the pans were filled and running over with water when the cylinder was opened. The average results obtained from crushing the three cubes and pulling two of the brickettes was:

Crushing Strength, pounds per square inch	6,181
Tensile Strength, pounds per square inch	554

Three more cubes and three more brickettes were then manufactured under strictly parallel conditions, except that *no alkali salts* or *chemicals* were used in the hardening cylinder. The average results obtained from crushing the three cubes, and pulling two brickettes were:

Crushing Strength, pounds per square inch	6,415
Tensile Strength, pounds per square inch	644

From the above results, it seems evident that the introduction of potassium and sodium salts into the hardening cylinder in the prescribed manner brings about no material *good* or *injury* to the brick. We may say then, that it occasions a slight increase in the cost of production, without any material gain in the quality of the product.

As has been stated earlier, there are three plants operating under the protection of this patent. One at Pittsburgh, Pa., one at Wilmington, N. C., and another at Sioux Falls, South Dakota.

The general practice at these plants is to mix ground lime and sand with the requisite amount of water to produce the proper consistency in a pug mill. The mixture is conveyed to bins where it is allowed to ripen for 24 to 48 hours, after which it passes through a second mixing machine of some sort, and on to the press. The Berg press is in use at Pittsburgh. The second mixing machine at the above named

place is a dry-pan, and by this procedure fairly even distribution of the lime was being obtained. A rather large hardening cylinder was being used here also—about six feet six inches in diameter by 66 or 67 feet long. I can see no reason why this mechanical treatment should not be slightly cheaper than the two preceding ones.

Patent 670299, March 19, 1901, granted to *Wilhelm Schwarz*, of Zurich, Switzerland. I will quote claim three which gives the essential features of the patent.

"The process of making artificial sandstone, which consists in drying the sand by heat *in vacuo*, then adding lime to the dry sand, and drying the lime, then mixing the whole and adding moisture all while under a vacuum."

The main object of this patent is to bring about accurate control of the moisture content of the raw brick. While this is desirable, I do not consider it essential, since my observation is that the workmen soon acquire sufficient skill to keep the moisture content of the mixture within the limits which will produce uniformly good brick. The *very small* amount of carbon dioxide which is eliminated by the machine being closed while mixing is in progress, is not worthy of any consideration.

In the opinion of the writer, the real merit of the Schwarz system lies in the mixing machine which Schwarz has devised to carry out his ideas, rather than in the patented process. This machine is described in Engineering News for February 19; 1903.

If this machine were divested of its complex vacuum and heating arrangements, I believe it would then be the best mixing device for the sand-brick industry which has yet been offered to the public. Since the total preparation of the raw material is brought about in one machine, it admits of simple plant construction, eliminating in a large measure conveying machinery which is a very desirable thing to do.

The Schwarz System Brick Company, of New York, are promoting this system, but as yet have no plants in operation.

Patent 663904, December 18, 1900, granted to *Peter*

Kleber, of Malatatt-Burbach, Germany. I quote the entire claim made by this patent.

"The herein described process for the production of artificial stone or brick, consisting in first mixing moist sand and unslaked lime so as to hydrate a portion of the lime only; second, adding sufficient water to hydrate the lime remaining unhydrated or unslaked, and allowing said mixture to stand sufficient to complete hydration; thirdly, bringing the mixture into a plastic cohesive condition by the addition of a minimum amount of water; molding said mixture into blocks and finally subjecting such blocks to the action of high pressure steam, substantially as described."

A careful study of this claim will show you that there is very little in it which is essential to sand-brick manufacture. No new principle is involved. Nothing can be gained by furnishing the moisture to the lime for hydration in two portions, instead of one; in fact the reverse is the case, since lime slakes best and most completly with a slight excess of water, such as would be needed to bring the entire mixture to the desirable condition for molding, after the lime had taken up what water it would. With some limes which are high in magnesia, it would be necessary to let the mixture stand at some stage after the addition of the water necessary for hydration, to give the slow-slaking magnesia time to complete its hydration before going to the press. With a hot, quick-slaking, or high-calcium lime, this would not be necessary; the hydration would be complete by the time the mixing had been thoroughly done, and the mixture could be put through the press and into the hardening cylinder while still warm from the heat generated from the slaking lime.

The Ohlemacher Brick Company, of Michigan City, Indiana, originally manufactured under the protection of this patent, but I do not believe in their present practice any just cause for action for infringement on the above Kleber patent could be found, were they inclined to abandon its protection.

The Michigan City plant is the pioneer plant in this country. The practice at this plant briefly stated is, to mix sand, ground quick-lime and water sufficient to completely slake the lime, and leave the mixture moist enough to mold

when finished. This is done in the first mixing machine. The mixture then passes through two more mixing machines, and screw conveyor, before going to the press. If the moisture content is not right, it is corrected in the last mixing machine by adding a little water, or a little dry lime and sand as the case may be.

The mixing machines are of the pug mill type, with many more paddles than are in an ordinary clay pug mill, The distribution of the lime was complete. The raw mixture is carried to a row of presses by an overhead drag conveyor, which has feed openings at each press, which can be closed when a press is not in use. The hardening cylinders are of normal size.

A properly equipped plant operated according to the last patent, or in the manner just described, should produce brick at minimum cost, since there is no extra handling of anything. The raw material starts at one end and comes out a finished product at the other end, with no delay except for the steam bath. A considerable portion of the heat, due to hydration of the lime is saved. Any other than a quick-slaking lime would make trouble however.

Summary.

I wish it to be understood that good brick can be produced under all of the last nine patents described, and that the value of each lies in its ability to reduce the cost of production, rather than in any advantage in producing the chemical reaction in hardening.

If the last five systems described, were all to work under exactly parallel conditions, I do not believe that the difference in cost of production would vary more than 35 cents per thousand, between the lowest and the highest. Likewise, the difference in cost of construction of the plants for each process will not vary more than a few thousand dollars under similar conditions.

The cost of plants will, of course, vary slightly from time to time with the rise and fall of hand and machine work, but will vary markedly with the locality at any time. A well equipped sand-brick plant, with a capacity of 20,000 bricks

in 10 to 12 hours, will cost, independent of site, from $20,000 $25,000 in Ohio.

The cost of production also will vary considerably with location. The cost of production in this country, independent of depreciation and interest on investment, varies from $2.50 to $4.00 per 1000. The selling price ranges in different localities from $8.00 to $15.00 per 1000.

From seven to eight million brick were made and sold in the United States in 1902.

It is a fact worthy of notice that of all the patents mentioned, only one was taken out by a citizen of the United States.

I see no valid reason why plants should not be built, or why good brick should not be made, independent of all the above mentioned patents or systems.

DISCUSSION.

Mr. Alfred Yates:—I think the gentleman who has presented this paper deserves credit for working it up in such detail. But, it is an innovation to expect a clay-worker to make brick from sand. I have heard no reference to the money end. It is the commercial end we are all looking at. If we cannot make money out of an industry, we naturally will not take hold of it. I notice Mr. Peppel recommends a press operating at fifteen or twenty thousand pounds per square inch. We have presses in this country running at eight or ten thousand pounds, and we think these are excessive pressures. I would like to ask him if he expects to install presses to work this increased pressure and still make a commercial success?

Mr. Peppel:—Certainly. Why not? I do not recommend more than fifteen thousand pounds to the square inch, and I should say that sand-lime brick presses now in operation are using between twelve thousand five hundred (12500) and fifteen thousand (15000) pounds per square inch. I don't believe anybody in the clay brick line is manufacturing with over seven thousand five hundred (7500) pounds to the square inch.

Mr. Yates:—We all know that clay is compressible. It

will reach a certain density, and when we arrive at that stage, it is elastic. But in my experience, whatever press may be used, there must always be a little margin left, so that if we get a little more clay in the mold, it will not break the machine. We have little vent holes to take care of it. What are you going to do, when you get a little more sand between the plungers than the space will admit?

Mr. Peppel:—That point is just what I brought out in my paper. I showed that the compression is very small beyond fifteen thousand pounds per square inch. Therefore, if you get a very little sand in the mold beyond that which is required to fill it at the normal pressure, you run up the pressure at an enormous rate, and possibly break the machine. This is a point which our American machine manufacturers have got to meet squarely before their presses will succeed in this new industry.

Mr. Yates:—I would like to ask, can this mechanical combination be brought into such dense form that this brick will be impervious to moisture?

Mr. Peppel:—Oh, no! The average absorption of moisture is about eight per cent.—it ranges from six to ten.

Mr. Yates:—The samples of this sand-lime brick which have been handed around here are very much like silica brick. I know that if a silica brick freezes, it is atomized. How do you expect these brick to stand frost, with eight or ten per cent of water in them? I am asking these questions because if there is more money in sand-lime brick than in clay brick, we want to know it.

Professor Edward Orton, Jr.:—Mr. Yates did not seem to gather during the reading of this paper, that Mr. Peppel made freezing and thawing tests 21 times in succession on the same bricks, and that after that treatment they actually stood more pressure than a similar set of bricks which were not frozen.

(Mr. Yates shakes his head, looks doubtful, and finally bursts into incredulous laughter. The humor of the situation strikes the audience, and general laughter results.)

The Chair:—There are one or two successful plants operating in this country on this line?

Mr. Peppel:—There are in this country five plants in operation, and machinery is bought for another one. In Germany there are several hundred plants in operation.

The Chair:—I assumed naturally that Mr. Peppel would not have taken the time to prepare all of this elaborate investigation on an up-in-the-atmosphere proposition. I gave him credit for that.

Mr. Yates:—I would like to ask the gentleman, if he knows whether any of these American plants have paid any dividends?

Mr. Peppel:—I am not familiar with the business management of these corporations, and do not know whether any of them have paid dividends or not. But the question as to whether they have paid dividends or not is premature, as they are all new and introducing a new product. We know what it costs to manufacture sand-lime brick. We know what they can be sold for; know what a plant costs; it is simply a question of ability to organize the business and to sell the product. They cannot help but make money, if they receive ordinary sound business management, and are operated by a man who knows the technical side thoroughly.

Professor H. A. Wheeler:—What are the figures?

Mr. Peppel:—I gave these figures a year ago in my first paper before this society, and a year's study of the question does not show that they ought to be changed. I thought then the cost of the brick would be approximately $4.00 per thousand. The figure I gave for the cost of a plant, independent of any royalty, was approximately fifty thousand dollars.

Professor Wheeler:—Will sand-lime bring the same prices as common building brick?

Mr. Peppel:—In different sections they are being sold at different prices. At one point they are sold at a little better price than common brick; at another place they are sold just a little bit under face brick. Their appearance would justify their going into the market about on a par with face brick. However, they can be made cheap enough to sell at par with common brick. The price they will sell at is a matter for the people going into the business

to decide for themselves. Eighty-five to ninety-five per cent. of the brick *can* be sold as face brick; the other part would simply be face brick with the corners knocked off, etc., in handling.

The Chair:—Have any abrasion tests been made?

Mr. Peppel:—No abrasion tests have been made. The abrasion test is never applied to building material so far as I know. It is used for comparing the toughness of material which is made to withstand wear, like paving brick. However, the tensile strength suggests in a measure, how the brick will wear in handling.

The Chair:—Were any of these bricks tested after the absorption test was made, while wet, to determine suitability for foundation work, where they would be constantly under water?

Mr. Peppel:—No, not by me, but some tests have been made in Germany, on the wet material, which show very slight differences; about the same proportionate difference which a clay brick usually shows when tested wet vs. dry. I don't mean vitrified brick, but ordinary building brick. We are not advocating sand-lime brick for pavers.

Professor Wheeler:—Have any attempts been made to color these brick?

Mr. Peppel:—They have been colored. This (showing sample) was made in an accidental way, and is not very beautiful.

Professor Wheeler:—Have any heat tests been made?

Mr. Peppel:—They have been heated to cone eight.

The Chair:—Have they been tested as a fire brick?

Mr. Peppel:—Not by me. My test merely consisted in placing them in the kiln and carrying them up to cone eight.

The Chair:—In direct contact with the fire gases?

Mr. Peppel:—They were in direct contact with the gases, but were not in the fire box. The Germans have made a number of tests. They built a small house out of the material, and built a wood fire around it, making a small sized conflagration; they claim that they came out in better shape than common brick. But I do not lay much stress on that test.

You cannot use this material as fire brick in a position where basic slags can come into contact with it. You can only class it as a fire-resisting material in such places as an ordinary silica fire brick would be desirable.

Professor Orton:—Do you think it will stand up with ordinary silica brick? Does it not contain too much lime?

Mr. Peppel.—It can be made with two per cent. lime. What is there to make it weak?

The Chair:—I had in mind the lining of muffles. I wondered if it could be used there.

Mr. Peppel:—This block (picking up one from the table) contains five per cent. of lime, and has been burned, but not up to the point where vitrification sets in. I think it was about to cone four.

Mr. Karl Langenbeck:—I think Mr. Stover's point is of interest to those connected with the clay industry proper. This particular application would not be in any place where it would come in contact with fuel, or any active chemical agent, as at the kiln mouth, but merely as slabs for lining the muffles. The question would be whether the hydrated silicate which forms the bond in sand-lime brick would pass into an igneous silicate bond, at cone eight or ten? What would be the influence of repeated heatings and coolings of such a product? That is the movement which racks such structure.

Mr. Peppel:—It would simply be the same as that of a silica fire brick, because when you bring sand-lime brick up to the point of vitrification, you simply make a silica brick of it.

Mr. Langenbeck:—The movement of silica under sufficient degree of heat is that of expansion, and possibly afterwards a slight contraction again. The question is, will this movement in this material probably assist in maintaining the structure, and make it preferable to the fire clay product, which we know contracts and in time racks? Are there any experiments with which you are familiar, or do you recollect about the behavior of the *Dinas* brick under heat?

Mr. Peppel:—I have no evidence to show, but I am of

the opinion that you have outlined the case correctly. The material is sufficiently porous to take up slight expansion in the very small amount of binding material; when the structure would reach the end of this ability to take care of expansion, the binding material would be in condition to flow. The expansion of this material at a little below cone thirty is reported from a German source to be about two per cent.

Mr. Langenbeck:—Then even with five per cent. of lime, it does not melt at cone thirty.

Mr. Yates:—I will inquire of Mr. Langenbeck if he considers five per cent. of lime added to free silica, sufficient to bring it to fusion at kiln heat?

Mr. Langenbeck:—No, I think not; but I am trying to get at just the point you are trying to get at—what would be the extreme limit of temperature which these brick would stand. We now hear that they did not fuse at cone thirty, and it is likely cone thirty-three before actual fusion takes place. This will give some rough idea of what we might expect under ordinary pottery conditions, at cone eight or ten. If, *without breaking down the structure*, the hydrated silicate of lime bond had passed into a igneous silicate of lime bond, and if actual fusion does not take place until you reach cone thirty or thirty-three, it looks as if it were an available fire-resisting material for certain parts of our kilns and muffles, with the promise that the movement which it undergoes is a less destructive movement than that of fire clay, with its continual shrinking under continued heat.

Mr. Yates:—I would further inquire of Mr. Langenbeck if he considers it will be a safe material to use, taking into consideration the expansion of silica? Would not the spalling and chipping of the silica brick be more destructive than the shrinking of the clay brick?

Mr. Langenbeck:—I fancy it would, and for that reason I put the question about expansion. Mr. Peppel has given his opinion, that while the total expansion of the silica is very small, as shown by tests, at such temperatures as interest us, say cone eight to ten, the expansive movement would

be taken up internally in the brick themselves and would not exert a total swelling force to amount to anything.

Professor Orton:—I think the discussion has taken a line which is probably most dangerous for sand-lime brick. I don't believe anybody has seriously put forth sand-lime brick as a suitable material to replace genuine *silica* brick. I do not see where any economy would result in using them. Where sand-lime brick of the *silica-brick* type are manufactured, they burn them at exceedingly high temperatures. They do not depend on any sintering bond, gotten at low heats. I sell cones to manufacturers of silica brick of that type, and theirs is almost the only demand I have for cones over number twenty. I had to specially make cones pretty near to the top of the series for these people.

Now, in brick made by this hydraulic process, with say twice or three times as much lime as is used in the normal silica-brick, why should we expect to destroy the hydrous silicate produced in hardening kettle, and replace it with an igneous silicate, without going up to high temperatures? This brick is put forth principally as a building material, and Mr. Peppel has shown us here today, the different qualities of sand and their effects, what impurities may safely be present, and how much. He has shown what kind of lime is best and the amounts which may be used; he has shown what pressures are necessary, both in the die and the steam cylinder. From my point of view, he has covered about all the phases of manufacture. Last year he showed us about how big an investment was necessary to get started. But, all this bears upon the production of tolerably cheap brick for building purposes. The question that seems to me most interesting, is where this particular kind of brick manufacture is most likely to take root to advantage.

Mr. Peppel:—While it would probably be possible to compete with clay brick, in the heart of the clay country, provided the sand and lime were at hand, I hardly think that in the next ten years we will see much encroachment upon clay territory by the sand-lime brick. The fuel consumption is very small, so it is desirable to try it first in

a locality where fuel is expensive. For that reason, those locations should be first selected where sand is abundant and fuel expensive. It certainly has the best chance there, not only to compete with clay bricks, but to get large prices for the product.

THE FORMATION TEMPERATURES OF CERTAIN SLAG SILICATES.

BY

PROFESSOR H. O. HOFMAN, PH. D.

The Chair: Gentlemen, we are to be favored this evening with a lecture upon a new phase of our field. At the earnest solicitations of the secretary, Dr. H. O. Hofman, Professor of Metallurgy in the Massachusetts Institute of Technology, has kindly consented to lay before us the results of his celebrated investigations on the "The Formation Temperatures of Certain Slag Silicates", and will show us the apparatus and methods he used in prosecuting his researches. I have the honor to introduce Dr. Hofman. (Applause.)

NOTE BY THE SECRETARY.

Professor Hofman, after making a few graceful introductory remarks, entered at once into the consideration of his subject. The subject matter and results have already been published in excellent form in the Transactions of the American Institute of Mining Engineers, Vol. 29, page 632.

The expense precludes their republication here, but those interested may procure reprints of the article by corresponding with Dr. Hofman or Dr. R. W. Raymond, Secretary of the American Institute of Mining Engineers, New York.

DISCUSSION.

Mr. Karl Langenbeck: Dr. Hofman, you say that all of your observations relate merely to formation temperatures and not at all to fluidity, and you mention about the difficulty of finding out anything about that factor. When we potters want to compare the fluidity of two glazes, we simply make cones of them and submit them to heat in a Seger furnace on a slab tilted at an angle of forty-five degrees. We see when they run down, which is most fusible. What objection would there be to employing that method with slags?

Dr. Hofman: The difficulty with slags in which iron forms a part of the base, is that some of the iron exposed to the air may be oxidized, and that changes its fusibility.

Some of the irregularities shown in my charts are due to changes from ferrous oxides to ferric.

Professor H. A. Wheeler: Were all these temperature observations on these diagrams made by means of Seger cones, Dr. Hofman, or with the Le Chatelier pyrometer?

Dr. Hofman: All were made with Seger cones. When I first began these experiments, I tried to use the Le Chatelier pyrometer. I took the slag mixture, and first put it in a platinum crucible and heated it. I found the platinum crucible converted into a carbide, and not being rich, we could not afford it. We tried another experiment, taking the Le Chatelier junction, and casing it around with some of the mixture, heating it carefully at first, increasing the temperature, and watching the increase of temperature. The point of retardation, or momentarily constant temperature shows the point when the silicate is formed. That formed a nice method of determining temperature, but the platinum wires would become brittle and break, and we had to give up the Le Chatelier pyrometer.

Professor Wheeler: You have not verified any of the Seger cones by means of Le Chatelier pyrometer?

Dr. Hofman: No. I accepted Cremer and Hecht for that. They have verified them. I think one is the melting point of silver, and the other that of an alloy of gold and platinum somewhere higher up. I forget just the temperatures, but there are one or two fixed points, I think, and between these two fixed points, a certain number of Seger cones have been interpolated. One melts after the other; and it is assumed that temperature intervals are equal. So, as I said before, in using Seger cones, if you want to be scientifically correct, you must leave out degrees centigrade, and give your results as occurring at Seger cone so and so. Degrees centigrade are only used to bring the results into comparison with pyrometers.

Professor Wheeler: To what do you attribute the irregularity of the curves?

Dr. Hofman: Do you mean in curve number four, singulo-silicate, where it makes a sudden jog? I cannot give any reason for that. Of course when this jog appeared, we

rather began to doubt, ourselves, whether that point was the real one, and I cannot just say how many experiments were made to settle it. Why it should go down here, and up there (indicating on chart), I do not know, but it is a fact that it does.

Professor Wheeler: Don't you think it is due to the irregular way in which Seger cones act?

Dr. Hofman: I do not think so, quite. I think any irregularity is not due so much to Seger cones, as to the fact that it is so difficult to keep ferrous oxide in a ferrous state. Take a mechanical mixture and form it into a chemical compound—if you get within fifteen or twenty degrees centigrade of the actual fusing temperature, I think you are working very closely.

Another point to be considered, is that the formation change of a mechanical mixture into a chemical compound is not simply a function of temperature. It is also a function of time. You will find somewhere of record (I think in Cremer), where a porcelain factory in Berlin, baked in two furnaces the same mixture of porcelain (I think I am quoting it correctly, tho it is a long time since I read the paper) and controlled the temperature with a Le Chatelier pyrometer. In one case, they fired in the normal way, with the regular rise of temperature until they reached the maximum, and then decreased the temperature in the normal way. They got up to a certain temperature and did it in a given time. The next time, for some reason or other the fireman did not fire regularly, and instead of having to fire to the same point to obtain the correct baking of the porcelain, they had to fire higher, thus showing on a large scale, in regular work, that this change of a mechanical mixture into a chemical compound is not simply a function of temperature, but time has something to do with it, and the method of firing, and the form of furnace has something to do with it.

Mr. Langenbeck: I think we are very much indebted to you for this expression of your views. We have waged quite a battle with Professor Wheeler on this point for several years, and he has tried to draw from you evidence to support his side. (Much laughter.)

Dr. Hofman: I do a great deal of work with the Le Chatelier pyrometer, in the melting point of alloys, etc. As soon as it is determined that a thing takes place at a definite temperature, there is nothing like the pyrometer; but the fusion of silicate takes place in a range of temperature.

Professor Wheeler: Dr. Hofman has not only come to my side, but there is the proof in black and white (pointing to the charts on the wall) of the trouble from the use of Seger cones.

Dr. Hofman: I disclaim that.

Mr. Langenbeck: I will ask Dr. Hofman whether there has been any work on this line, running more into the acid silicates? Our interests as ceramists, are mainly with acid silicates—little or nothing with basic silicates.

Dr. Hofman: As far as I know, no other work of this kind has been done, in which iron forms one of the bases. As I said in the beginning, Professor Akerman, of the Royal School of Mines in Sweden, has done splendid work on the blast furnace slags or the silicates of alumina and lime. I cannot recall off-hand how far he carried it, but his paper has been translated into several languages—we have it down stairs.

Mr. Langenbeck: Another question. Of course, under the line of your work in formation of slags attendant upon the reduction of metals, it is only the form of ferrous silicates that interests you. At the same time, I would like to ask if you have done any other work which would probably give some general information on the presence of ferric, as well as ferrous compounds? It seems to me that in testing the refractoriness of clay containing more or less iron, that it would be important in stating comparisons against Seger cones to mention whether under oxidizing or reducing conditions: otherwise, the comparisons would be of comparatively little value. Isn't that the case, or don't you think that it makes much difference as to whether the iron is ferrous or ferric?

Dr. Hofman: The ordinary fireclays contains such comparatively small amounts, I doubt whether it has a decided effect. I do not think it would have a decided effect. In

the laboratory work here in fire-clays, we use the DeVille furnace, and of course the clay is surrounded entirely with gas-carbon, and I do not think there can be any strong oxidizing reactions taking place. It may be a different thing when put into an open furnace and tested there.

Professor Edward Orton, Jr: It seems to me that Dr. Hofman has done this society a great service in presenting this phase of silicate formation to our attention. I have persistently taken the attitude during the formative years of the society, that we represent the whole field of silicate industry. We have brought into the organization not only the potter and the brickmaker, but we have also ensnared the cementmaker, and now for the first time, we have had an address upon a phase of silicate formation, the point where our sphere touches that of the metallurgist. Dr. Hofman's contribution should be especially welcomed on that account.

I have listened with exceeding pleasure to Dr. Hofman's address tonight. My own experience in making fusible glasses, concerning which I read a paper a year ago, confirms the general character of his curves but at a very much higher stage of silicate formation. I was dealing with acid glasses, while he was dealing with basic ferro-calcic silicates. His plane of operation is below mine, but if I could plat the two curves, they would be substantially parallel.

Dr. Hofman: Professor Akerman's curve is similar to that one—so there are three.

Professor Orton: I made a series of glasses last year and found that with what in your method of expression would be a five-fold silicate, I had ordinary window glass. By reducing its acidity to four, it reaches a slightly more fusible stage. By reducing to three, we get approximately about the same fusibility as four-silicate; reducing further the curve began to go upward again as yours there does, tho your series and mine were separated by a wide difference of temperature.

Where the curve makes zigzags like that after repeated trials, I would like to ask whether you think it fair to say it is due to the mass of the material entering into the formation of definite silicates, at the low point of the curve, and to the

ratios being such that there is a good deal of material left over in other cases, which does not enter into combination, and thus causes the high points of the curve?

Dr. Hofman: This is a question of solution. We now generally look at slags as solutions of one silicate in another; so if a slag is composed of one silicate dissolved in another, we obtain low fusion temperatures; and when we get an excess of either acid or base, it does not so readily dissolve and hence causes irregularities. So where we have these irregularities in the curve, we think the lowest points may be reached by the joint solution of two silicates, and the higher points may be the only mixture of the two silicates.

Professor Orton: These curves of Professor Hofman's slags, seems to me to have a definite bearing on the subject discussed yesterday morning, viz., the formation of matt glazes. When we fuse up a mixture for making a matt glaze, it is not certain we shall produce a compound which will crystallize well. But if the theory that the formation of matt glazes is due to compounds which readily crystallize be true, then it seems likely that there are certain points between acidity and basicity in the composition of the glaze exceptionally favorable for the production of this crystallizing silicate. Those points may be indicated by such dips or elevations as those in these curves. Other points between the same two extremes might not give a good matt. Those who produce matt glazes in a commercial way, state that the range of composition and temperature within which they may be produced satisfactorily is exceedingly small. That is, you must get scientifically or empirically at one of the points where some particular mineral in solution in the glaze will crystallize out easily and rapidly and with such a size of crystal as will give the soft silky texture and sheen which the good matt shows. Otherwise, you may get a glaze which is matt in one sense, *i. e.*, not bright nor glassy, but which is simply immature, or dull from the segregation of matter either insoluble in the other silicates of the glaze, or which

is cast out from solution, without crystallizing, as amorphous separations.

On motion, the president extended the thanks of the society to Dr. Hofman for the presentation of a lecture in which the members had found so much interest and which was so pregnant with lines of profitable thought and investigation.

"THE STRUCTURE OF SILICATE MIXTURES."*

DISCUSSION BY A. V. BLEININGER, B. SC.

The note on "The Structure of Silicate Mixtures," by H. E. Ashley, touches on a point which is of the greatest interest to the ceramist. We all realize, I believe, the deficiencies of purely chemical research and it must be our aim to supplement the gaps left by chemical work, with physical methods along lines similar to those followed by the metallurgist and using the means offered by physical chemistry and mineralogy. It will, perhaps, not be out of place to look over some of the scientific equipment now available for the attacks of the problem of the constitution of the silicates. We have at our disposal the following physico-chemical methods of investigation:

1. The determination of melting points.
2. Microscopic and mineralogical examination.
3. Thermo-reactions of neutralization, solution, hydration and determination of specific heats.
4. Determination of water of hydration.
5. Velocity of reaction.
6. Optical properties.
7. Solving power of liquid silicates.
8. Partial solution of silicates by re-agents.
9. Determination of density, elasticity, tensile strength, crushing strength and hardness.
10. Co-efficient of expansion.
11. Electrical properties.

Melting point determinations of silicates, especially of slags, have been made in great number and some valuable information has been drawn from them as is shown by the work of Akerman, Hofman,[1] H. E. Ashley[2] and Jüptner.[3]

This work is capable of great extension, especially since

*Original paper published in Trans-Am. Ceramic Society, Vol. IV.

[1] Transactions American Institute of Mining Engineers, Vol. 29, p 682.

[2] Transactions American Institute of Mining Engineers, Vol. 31, p 854.

[3] Siderology, The Science of Iron. Hanns Freiherr Von Juptner, translated by Charles Salter, 1902.

electric furnaces are becoming a recognized part of mineral laboratories, thus eliminating the factor introduced by the fire gases. The work done by several members of this society (Prof. Orton, Mr. Purdy) illustrates this point very clearly.

Microscopic examination also offers a vast and exceedingly fertile field, which should be cultivated much more than it is. It is and must be intimately associated with mineralogy. Already in the examination of raw materials its great importance is shown. Many problems can only be solved with the aid of the microscope. The character of many clays can be fixed definitely only by means of it. In fact, the application of the microscope has advanced to such a stage that it has been suggested by an eminent authority, Prof. Rosenbusch, as a means of analyzing rocks quantitatively in thin sections, using glass slides provided with fine cross-lines which divides the surface into squares. The area occupied by each mineral is estimated by means of a simple calculation, and in this way the rock is analyzed quantatively for its mineral constituents.

The qualitative examination of crystals produced from silicate mixtures is well illustrated in a paper by W. Jackson and E. M. Rich.[1] in which is shown a number of microphotographs of crystals produced on the surface of different glasses by etching with dilute hydrofluoric acid, which bring about partial solution. It seems a pity that these investigators did not go further into this study of annealing the glasses for longer or shorter periods, thus producing crystals in greater numbers and variety. Take for instance, the hard glass tube of a carbon combustion furnace; after being heated for some time, the glass gradually de-vitrifies and finally assumes a porcelain-like appearance.

It does not seem probable to the writer that mere condensation of vapors on glass surfaces will give a satisfactory picture of the micro-structure, since too many surface phenomena are liable to interfere, and since the surface itself does not represent the structure of the main mass.

Several years ago, I made a thin section of a paving

[1] Journal Society Chemical Industry, Vol. XX, p 555, 1901.

brick specimen collected by Prof. Orton, which showed in a remarkable manner three zones of vitrification, 1st, good, sound vitrification with red color; 2nd, over-vitrification, accompanied with dark color, and 3rd, the beginning of vesicular vitrification. Examined under the microscope, the zone of over-vitrification was distinctly indicated by the formation of needle-like crystals, which however I did not succeed in identifying.

Another use of the crystallographic examination is represented by the work of Dr. Schott, who in the eighties, examined fused solutions under the microscope, allowing them to crystalize out and observing the crystalization in its very genesis. By means of a gas flame and suitable shields he kept the solution at a red heat and thus was able to regulate the cooling and heating up at will; he was thus able to redissolve crystals noting their relative melting points. In this way he could study igneous reactions which often differ radically from wet reactions involving the same substances. Now when we have at our disposal, electric furnaces of all kinds, it would seem a very easy matter to maintain any desired temperature.

The determination of specific heats should, in the nature of the case, give valuable constants, and could be applied without great experimental difficulties. These heats of reaction and neutralization as applied to cements, and soluble silicates in general, have been used by several experimentors and always produce valuable comparative constants. An example of this is the testing of lime by means of the calorimeter in which the heat evolved on hydration or by solution offers a rapid commercial method.

The determination of the water of hydration is applicable to clays as well as to cements; in the former it is a well known fact that this furnishes an index of the purity of clay. In testing trass for cement-making, the content of combined water is made a point of commercial importance. In cements, the hydration values proved valuable supplementary evidence.

The velocity of reaction is applicable to clays and glazes only in a limited degree, in regard to the rapidity of

fusion. For cements, the velocity of the hydration reaction is of great importance, and divides cements into large characteristic classes.

The optical properties of glass, the indices of refraction and dispersion have been examined quite thoroughly by Schott, and his associates at Jena, with reference to the ratios of different bases in the composition, but I do not believe that the acidity and the effects of systematic additions of alumina as applied in glazes have been studied from this standpoint. It might be possible that the application of the Lorenz formula could throw light on questions of constitution.

Polarization, of course, properly comes under the head of mineralogical examination, where it is constantly used. Colorimetric examinations (see Ostwald Physiko-Chemische Messungen, page 246) should be applied extensively for color reactions and phenomena in glasses and glazes.

The solving power of silicates in igneous fusion for various reagents could be made a valuable feature in ceramic work, since chemistry as a whole is becoming more and more a question of solubility. For instance, the solving power of definite glasses for certain bases, like lime, or acids, like tin oxide, at certain temperatures must be a function of the acid-base ratio.

Partial solution has already been illustrated by citing the work of Jackson and Rich, who used hydrofluoric acid to etch glass. A large number of liquids are available for this purpose.

The determination of the physical properties hardness, tensile strength, density, elasticity, crushing strength, etc., considers properties whose importance for the examination of certain bodies depends of course on the particular substances under discussion and the purpose of the examination. Messrs. Jackson and Rich made use of the difference in density in endeavoring to separate the different constituents of the extremely fine ground glass, assuming that the glass is a mixture of various silicates more or less homogeneous, according to the views of Benrath. This they did by means of the Schoene funnel and the Thoulet solution, a suspension

method using a methyl iodide solution of different density, whereby some constituents would float and others sink. The probability is that the work was not successful, and it would perhaps have been better if the glass had been annealed to produce crystallization. In this connection, it might be mentioned that Daubree[1] already has shown that ordinary glass is decomposed by superheated steam into quartz, wollastonite and alkaline silicates.

An interesting study suggested would be the investigation of the density of porcelain at various stages of burning.

The expansion of solids by heat, the co-efficient of expansion of glass as well as other ceramic bodies, and the rate of expansion for rising or falling temperatures promises to give valuable constants, the difficulty being, however, the extremely delicate measurements and the great amount of time consumed in this work.

The least promising physical data are perhaps based on electrical phenomena, electrical resistance and the study of magnetic fields produced by electro-magnets. A number of years ago the writer did some work in separating grains of iron pyrites from dried clay, by means of an intense magnetic field. Though the experiments were not completed, they were successful as far as they went.

This little summary is intended to indicate the present scope of the available physical-chemical methods, for one must remember that theoretical results are not proven by one set of constants, but it requires several coincident experimental factors. At the same time, we should realize the limitations of the methods, as well as of the material to be examined. For instance, microscopic examinations of soft burnt clay will reveal but little and should not be expected to furnish important data.

[1] Ann. des Mines, Series V. No. 12, 1857.

THE WORK OF THE CERAMIC ENGINEER IN THE BRICK-MAKING INDUSTRY.

BY

WILLARD D. RICHARDSON, A. M., COLUMBUS, O.

There is constantly increasing evidence that manufacturing businesses are becoming more and more dependent for success upon engineering. Engineering is applied science, and all business, especially all manufacturing business, is reducible to a scientific system, and its operations to certain definite scientific laws. It is the work of the engineer to ascertain these laws and apply them successfully to every special case under his charge. The commercial value of an engineering education is becoming more generally appreciated by business men. The growing popularity of engineering schools and the constant extension of engineering courses is a marked feature of our recent educational development and is certain to be far reaching in its influence upon the industrial progress of America.

Clay-working, one of the oldest and most important of the practical arts, is one of the latest to receive the benefit of scientific instruction. Legislators have only recently been brought to realize the industrial importance of the ceramic arts and to make appropriations for ceramic departments at some of our state universities. The ceramic engineer has in this country only just come upon the field, and his labors so far have been given chiefly to pottery and the more artistic forms of clay-working. To arouse greater interest in the need of the services of the ceramic engineer in the brick-making industry is the object of this short paper before our society. In the brick-making industry I include for this purpose not only all forms of building brick, paving brick and fire brick, but also drain tile, sewer pipe, roofing tile and terra cotta.

The large loss of money in the brick business is notorious. There is hardly a community that has not experienced

some failure or waste of capital in brick-making enterprises. In consequence even legitimate projects in this line are looked upon with suspicion and often cannot secure the confidence of investors, and thus a barrier is placed to the healthy development of this industry. Of course, no means can be found that will entirely prevent unsound ventures in any business, but a large majority of the failures in the brick business can and should be prevented through the agency of the consulting ceramic engineer.

Brick plants are often established without good reason, without such investigation as it would seem that ordinary business sagacity would require. They are perhaps located where the clays are too limited in quantity and too varying in quality, or practically inaccessible, the cost of mining being excessive, or not suitable for the product desired; or where the facilities for manufacture are unfavorable or the market inadequate or remote. Or the yard may have been improperly planned and equipped, and employing a process for which the clays are not adapted or against which there is a prejudice in the market. Or the machinery, dryers and kilns are not such as should have been selected for the most satisfactory and economical results. In fact the whole establishment shows a lack of technical knowlege that should have been supplied by the ceramic engineer. Had he been consulted, perhaps he might have advised after a preliminary investigation, the abandonment of the undertaking on the ground that the conditions were not favorable for profitable investment. Or, after exploiting and testing the clays and carefully examining all the conditions, his favorable report would have secured him a commission to make complete plans and specifications for the construction of a plant; and so well would he have fulfilled this commission that the success of the enterprise would have been assured. His fees for this engineering work would amount to a very small percentage of the cost of the plant, and would not only not have increased the cost of construction, but his services in preparing definite plans and specifications upon which competitive bids could be secured, would have reduced the total cost by more than the amount of his fees.

The ceramic engineer will frequently be called upon to correct faults of manufacture, to establish more economical methods and to effect such a reorganization as will place the plant upon a paying basis. Sometimes it is true he may be called in too late when the money is all gone, the property mortgaged and no means can be found to apply the necessary remedy. Had he been called in a year or two earlier, he might have prevented the loss of several thousands of dollars, but at that time perhaps the projectors were so confident of success, and of the sufficiency of their own knowledge, that they would have been unwilling to pay a few hundred dollars for the services of an engineer.

A competent consulting engineer should be a man who has not only pursued and completed a scientific course of study especially applied to the clay-working industries, but who has had also considerable practical experience in manufacturing clay products. He should be able to exploit and test clays, and advise the best methods of working, to design factories, dryers and kilns, and to specify the proper machinery. He should also be able to remodel and reorganize old plants and wrest success from failure wherever possible.

Under present conditions it is easier to outline the work of the ceramic engineer than it is to assure him of such employment. However beneficial might be the services of the ceramic engineer to the brick manufacturer, it is not to be expected that the opportunity for such service will be readily afforded. Brick manufacturers in this country, and especially those about to engage in new enterprises, are not yet educated up to the importance from a practical business standpoint of employing a consulting engineer to investigate their propositions, or faults of manufacture, or to specify improvements in their methods. This has come about only slowly in other industries and will doubtless be of slow development in ours. So that while there is a splendid field of labor for the consulting ceramic engineer in the brick-making industry, he cannot as yet be assured of remunerative employment. And the ceramic engineer I suppose, like all other consulting engineers, must needs have a code of ethics that would prevent any active solicitation for clients. At least

such solicitation would be undignified and distasteful to a man of education and refinement, however much he might thereby extend his usefulness. But at any rate, it must be in his code not to solicit nor accept commissions from anyone on account of labor or material furnished under his specifications or directions. This is good morals for others, as well as for engineers.

Graduates of ceramic schools will not be likely to assume at once the profession of consulting engineer, and should not be encouraged to do so until they have had several years experience in practical operations. But it is from this class of men that engineers for the brick-making industry are to come. This has been the result of technical education in Germany. Ceramic schools established there long ago, have produced a class of engineers that have devoted themselves to brick-making, and by their labors this industry has made such progress in the solution of technical problems, has been brought under such control, has been made commercially so sound and profitable, as to incite the emulation of all progressive brick-makers everywhere. With them, brick-making is no longer an empirical art but an established science. The construction of brick work is not with them a haphazard matter, a "rule-of-thumb" procedure, but a carefully planned and accurately calculated undertaking. All operations of manufacture are conducted according to established scienctific principles. The result is a product not only adapted for the purpose for which it is to be used, but one that has been economically made, thus insuring a profitable investment.

Such will be the results in this country of the educational movement now in progress. Unsound brick-making projects, improper equipment and wasteful methods will come under the control of the ceramic engineer. We now undoubtedly lead the world in the efficiency of our brick-making machinery, but in accurate technical knowledge of clays, and the best methods of treating them for special purposes, in a scientific system of drying and burning, in fact in all the chemical processes involved in the manufacture of clay products we have much to learn, and there is only one

way to learn it, and that is by the training of our young men in technical schools, giving them a thorough course in ceramic engineering. The rest will follow. Such of these men as enter the brick-making industry, will gradually bring about a more scientific system, that will give more positive and certain results, a better product at less cost, a business with less risk.

The time will come when few brick plants of any pretensions will be built without the advice and assistance of the ceramic engineer. He will be engaged at the start to exploit the clay deposits, make analysis of the clays and practical demonstration of their value. He will also examine all the conditions that have a practical bearing upon the proposed establishment. His report upon all these points will determine the action to be taken. If he reports favorably, and recommends the project, the next thing is to prepare plans and specifications for the complete plant, having in view the nature of the material, the kind of product desired, and the amount of capital to be invested. This will call for his best skill and judgment, as upon it depends largely the success of the whole business. He will supervise the construction and starting of the plant, and give instruction in all the operations of making, drying and burning. He will act as consulting engineer in investigating and correcting any faults or difficulties of manufacture that may arise. This in brief is the work of the ceramic engineer in the brick-making industry; to give to it his time, his energies and a mind specially trained for the study and solution of ceramic problems, and thoroughly alive to the importance and to the possibilities of the brick-maker's art. Through his agency alone, the first quarter of the 20th century will witness such advancement in the art of brick-making, such improvement of all conditions of manufacture, such an elevation of the financial standing and social status of the brick-maker as will give to brick-making a foremost place among the world's industries.

NOTES ON THE CONSTITUTION OF CHROME-TIN PINK.

Discussion by Owen Carter.*

Poole, England.

Referring to Mr. Hull's interesting paper in Vol. IV of the Transactions, on the "Constitution of Chromium-Tin Pink", I would beg to submit the following notes. I fear that my remarks on this subject will not be as suitable as I could wish, owing to the fact that we English potters fire our Majolica glazes, colored glazes or enamels, as they are variously called, at a lower heat than our American friends appear to do. Again, I am not quite sure if the color Mr. Hull was working upon was of the same kind as the piece I enclose,[1] and propose speaking of, which in England is known as "Sang de Boeuf," a very popular color and considerably in demand. There are of course innumerable chromium-tin shades and colors, but this deep, rich tint was that with which we had most trouble, and may, I think, be taken as more or less representative of the whole group, even though the maturing point of the glazes be different.

I understand that Mr. Hull's experiments were conducted with the object of gaining information:

Firstly. As to the most favorable composition of the pink frit, and

Secondly. What type of low fire glaze developes the color to the best advantage.

With regard to the first question I do not think it much matters what formula one takes, provided it is one of the many that will make a decent strong pink, crimson, or

*Read by title at Boston meeting. Further discussion specially invited.

[1]Note by the Secretary. Mr. Carter sent with his paper several small shards glazed very handsomely with one of the finest chrome-tin red glazes it has ever been his fortune to see.

maroon underglaze color. What the exact tint may be when used as an underglaze color can hardly matter in the least, as when it comes to be mixed with the glaze, its proportions are entirely upset. We use the following for the pink frit:

26 parts oxide of tin.
14 parts whiting.
1 part bichromate of potash.

thoroughly mixed and calcined in the hardest place in our vitreous kiln.

The second question is, in my opinion, the all important one. I am ashamed to think now, of the many trials made and the time they took, not to speak of the trade lost, before we succeeded, and all because we did not realize the importance of this second question of Mr. Hull's, Some times (probably because the heat was by chance just suitable) we would get fair results, and feel sure we must be on the right track, but on trying again the same recipe, the color would be either not developed or gone entirely, because probably the exact heat had not been hit upon, and such an exactness of temperature was in practice impossible. This sort of thing is far worse than downright failure, for it keeps one hanging on and wasting time. At last, it dawned upon us that the trouble might be in the glaze, so we took two frits rich in lime and silica, one alkaline and the other a soft lead frit,

Alkaline Frit.		Soft Lead Frit.	
Borax	150	Litharge	240
Flint	75	Cornwall stone	90
China clay	50	Flint	50
Whiting	50	Whiting	10

mixing them with the pink underglaze color thus:

	A	B	C	D	E	F	G
Soft lead frit	30	25	20	15	10	5	..
Alkaline frit	..	5	10	15	20	25	30
Pink underglaze	2	2	2	2	2	2	2

These were fired at cone 09, the results being as follows:

A. Rich mellow red, but rather too brown, hardly life enough, but still a beautiful color.
B. A little more red than A.
C. } Beautiful bright crimsons.
D. }
E. Good crimson but decided tint of purple.
F. A stronger tint of undesirable purple.
G. Disagreeable bluish purple color.

Some delay was now occasioned by "A" being the most mellow and artistic shade, and, thinking a little more fire would develope a brighter color, we made more experiments on this line. But it was soon discovered that it required too exact firing for practical purposes and that when "C" and "D" would be still bright and good, "A" would be spoilt entirely. Then we tried a harder lead frit for "A," still using no alkaline frit, the result, though better, was still unsatisfactory in the same way as before. It was therefore decided to try and make "C" and "D" more mellow with chromate of lead, which proved successful. The following frit was then constructed which will be seen to be 100 parts of the soft lead frit; 60 parts of the alkaline frit:

Borax	90	Frit at 09 cone, grind and dip without admixture of any raw material.
Flint	95	
China clay	30	
Whiting	40	
Litharge	240	
Cornwall stone	90	We wash neither the under-glaze color nor the frit, but it might be better if this were done.
Maroon underglaze	29	
Chromate of lead	6	
	620	

Small charges of this color were fritted in flinted saggers in front of enamel kilns at 09, and thorough trials were made in different kilns. It was found to stand slight variations of heat better than we had dared to hope; the color also, seemed to be the popular shade. No further alteration in the recipe was then made, and the formula now stands as above, some tons of frit having since been made from it. This method of calcining in saggers in the fronts of enamel kilns was soon found inadequate, as the color was selling too well to keep going in this way. We therefore

thought we would try fritting it in the crucible kiln, the crucibles being fed at the top, and the molten frit running out into water through a hole in the bottom of the crucible. The type I mean is of course well known to you all. What was my horror when walking round the works a day or so after this was decided on, to see the crucible kiln in full swing, and a bright grass-green frit in the casks, which I was told was " Sang de Boeuf." Needless to say, I stopped the fritting at once, had some frit ground, and trials of it got in the kilns with as little delay as possible. I fully expected them to come out a bright green like the frit, but to my surprise and delight, they were, if anything, a brighter and better red than tiles dipped from frit which had been calcined in saggers.

Thus ended our troubles, up to the present, with this particular color, and if the narration of our fruitless labor and the way success was attained, will help our fellow potters, we shall be more than glad. The recipe is probably capable of improvement, but in a pottery there are so many things to do that one can only spare time for the most urgent.

Discussion by Otto Hensel,
New Lexington, Ohio.

An attractive red glaze, with a tinge of yellow, or at least without trace of the ordinary purplish color being very desirable in terra cotta effects, I made some experiments in trying to obtain it by the use of tin, chrome, and lime.

The body was ferruginous and quite high in alkaline earths. The only kilns available for fritting the color and firing the glaze were the ordinary down-draft, and the Stewart kiln, a modification of the down-draft, wherein the fire-gases pass through flues under the solid floor, up through bags or flash-walls on the opposite sides respsctively, then down through the setting and out through small flues near the bottom in the walls of the other two sides. Oil was used for fuel.

The most remarkable oxidizing conditions appeared to prevail on the floor and for several feet up in these solid-bottom kilns. Almost any haphazard mixture of the ingredients required for pink and the allied reds would give beautful clear glazes of a desirable color. I may add that the glaze was put on the raw body, and had to undergo the slow firing required for green ware. The above circumstance lured me into an unproductive attempt to use the tin-chrome formulae under down-draft firing conditions. The solid-bottom Stewart kilns were altered to ordinary down-draft in the course of my work.

At first, color batches were fritted on the floor of the solid-bottom kilns, where a temperature probably equal to Cones 04 and 03 was reach. Pulverizing and a second firitting was found to produce much more stability and strength of color in the glaze. An intermediate washing also improved the color to some extent.

The first series of colors produced very fine, almost direct reds, under oxidizing conditions, but were badly reduced otherwise. The best of this series were:

$$1\quad \left.\begin{matrix}0.03\ K_2O\\0.07\ Na_2O\\0.40\ CaO\end{matrix}\right\}\ \left.\begin{matrix}0.03\ Al_2O_3\\0.002\ CrO_3\end{matrix}\right\}\ \left.\begin{matrix}1.00\ SiO_2\\0.14\ B_2O_3\end{matrix}\right\} + 0.08\ SnO_2$$

$$2\quad \left.\begin{matrix}0.03\ K_2O\\0.05\ Na_2O\\0.42\ CaO\end{matrix}\right\}\ \left.\begin{matrix}0.03\ Al_2O_3\\0.003\ CrO_3\end{matrix}\right\}\ \left.\begin{matrix}0.70\ SiO_2\\0.10\ B_2O_3\end{matrix}\right\} + 0.08\ SnO_2$$

In the amounts given here, they were added in a glaze in which the RO including these given, footed up 1.00. The first color gave a fine deep red, lead being 0.44 equivalents in a medium hard glaze. Even when reduced, the reduction was not complete. The second color with somewhat less spar and 0.48 equivalent lead gave a beautiful yellowish red, a sort of crimson, and proved rather stable under reducing conditions.

The formulae given by Seger in his article on underglaze colors, such as,

$$3\quad \left.\begin{matrix}0.032\ Na_2O\\0.750\ CaO\end{matrix}\right\}\ 0.03\ CrO_3\ \left\{\begin{matrix}0.900\ SiO_2\\0.064\ B_2O_3\end{matrix}\right. + 1.00\ SnO_2$$

$$4\quad \left.\begin{matrix}0.023\ Na_2O\\0.840\ CaO\end{matrix}\right\}\ 0.01\ CrO_3\ \left\{\begin{matrix}1.780\ SiO_2\\0.047\ B_2O_3\end{matrix}\right. + 1.00\ SnO_2$$

$$5\quad \left.\begin{matrix}0.033\ Na_2O\\0.750\ CaO\end{matrix}\right\}\ 0.023\ CrO_3\ \left\{\begin{matrix}1.410\ SiO_2\\0.066\ B_2O_3\end{matrix}\right. + 1.00\ SnO_2$$

were next tried.

These colors gave their finest results in glazes in which the RO was composed as follows:

Lead—About 0.50 equivalents, although it went to 0.63 in one fine glaze, in which one-eighth of color number 3 was mixed so as to have the following total composition:

$$\left.\begin{matrix}0.630\ PbO\\0.314\ CaO\\0.054\ KNaO\end{matrix}\right\}\ \left\{\begin{matrix}0.15\ Al_2O_3\\0.004\ CrO_3\end{matrix}\right\}\ \left\{\begin{matrix}1.792\ SiO_2\\0.108\ B_2O_3\end{matrix}\right\} + 0.125\ SnO_2$$

This glaze showed some bubbling, due most likely to low alumina. The red developed well in this glaze, though it was very susceptible to reduction. Aside from the color and some quicklime, all the ingredients used here were raw.

Soda—Inclusive of what little spar I could use, 0.25 equivalents, or less. High soda was conducive to stability, and produced more yellowish effects as against the purplish of high lime.

Potash—As carbonate or nitrate, gave a more pleasing color than soda, but in the few trials that I made, I found the glaze rather more susceptible to reduction.

Lime—Had to be as high as 0.25 to 0.36 equivalents.

Zinc—Was found to be of no service.

Boric Acid—0.10 equivalents, although a very beautiful deep purple was obtained with 0.16 equivalents.

The next experiment tried was a series of colors to see what good would come of the incorporation into the color frit of all the elements required in the development of color under our conditions. The frits were fired in the kiln along with the ware, at about Cone 07.

The following formulae show what part of the glaze, whose total RO equals unity, was fritted as the color-introducing compound:

$$6\quad \left.\begin{matrix}0.03\ K_2O\\0.12\ Na_2O\\0.42\ CaO\end{matrix}\right\}\ \left\{\begin{matrix}0.03\ Al_2O_3\\0.002\ CrO_3\end{matrix}\right\}\ \left\{\begin{matrix}0.70\ SiO_2\\0.10\ B_2O_3\end{matrix}\right\}\ 0.096\ SnO_2$$

$$7\quad \left.\begin{matrix}0.03\ K_2O\\0.14\ Na_2O\\0.37\ CaO\end{matrix}\right\}\ \left\{\begin{matrix}0.03\ Al_2O_3\\0.0025\ CrO_3\end{matrix}\right\}\ \left\{\begin{matrix}0.60\ SiO_2\\0.07\ B_2O_3\end{matrix}\right\} + 0.107\ SnO_2$$

$$8\quad \left.\begin{matrix}0.02\ K_2O\\0.05\ Na_2O\\0.25\ CaO\end{matrix}\right\}\ \left\{\begin{matrix}0.02\ Al_2O_3\\0.002\ CrO_3\end{matrix}\right\}\ \left\{\begin{matrix}0.53\ SiO_2\\0.06\ B_2O_3\end{matrix}\right\} + 0.107\ SnO_2$$

Of these three color-frits, number 6, while less stable under reducing influences than those colors based on Seger's

underglaze reds, appeared to give the most desirable effect in terra cotta work of any in my list.

Number seven appears as a slightly more pleasing color effect, though it seemed to a small degree less stable. Number eight gave a quite direct red.

The Stewart kilns having been remodeled during these tests by taking out their closed bottoms, and thus converting them into ordinary down-drafts, it became much more difficult to get purely oxidizing conditions. The colors had now to be fritted in the middle of the setting. In order to make them at all serviceable, the borax had to be increased, thus adding to the stability but detracting from the pleasing tone of the color.

In experimenting to find how much boric acid must be added to meet this change in conditions, I found the two following most stable:

$$9 \quad \left.\begin{matrix} 0.075\ Na_2O \\ 0.840\ CaO \end{matrix}\right\} \ 0.014\ CrO_3 \ \left\{\begin{matrix} 0.94\ SiO_2 \\ 0.15\ B_2O_3 \end{matrix}\right. + 1.00\ SnO_2$$

$$10 \quad \left.\begin{matrix} 0.100\ Na_2O \\ 0.840\ CaO \end{matrix}\right\} \ 0.014\ CrO_3 \ \left\{\begin{matrix} 0.780\ SiO_2 \\ 0.200\ B_2O_3 \end{matrix}\right. + 1.00\ SnO_2$$

Reduction of lime showed weakness of color, from lack of development or reduction.

The introduction of barium to the glaze seemed to give great promise at first, for a content as high as 0.14 equivalents in the glaze appeared to make the color absolutely proof against reducing influences, but a counter trouble arose at once from infusibility of the glaze. When it happened that the ware was rather over-fired at top, a very fine direct red was the result; but in the middle of the kiln the glaze appeared rough and dead, besides being of a bluish purple tinge. Fritting of barium did not seem to help matters any. The addition of 0.06 to 0.08 equivalents did not seem to alter the shade so very much, though it added materially to the stability of the color.

The use of an engobe, under the glaze, was not resorted to very extensively, as I had not at that time worked out a first-class composition. Some trials were made with an engobe specially prepared to aid the glaze to resist reduction, and a great improvement was noted. Barium again was the

most powerful agent, but even without it, the results showed improvement. The best composition was as follows:

$$11 \quad \left.\begin{matrix} 0.50\ Na_2O \\ 0.10\ K_2O \\ 0.20\ BaO \\ 0.20\ CaO \end{matrix}\right\} \quad 0.35\ Al_2O_3 \quad \left\{\begin{matrix} 3.50\ SiO_2 \\ 0.20\ B_2O_3 \end{matrix}\right.$$

This engobe required a frit, as did all the other serviceable ones.

This closed my experimental work on this interesting subject. I had succeeded in producing a stable red glaze at our heat and under our firing conditions, but it was not of a very attractive or desirable color. It is possible that the low temperatures at which I had to work both for fritting and fusing the glazes made the task peculiarly difficult.

My experiments seemed to me to be reasonably complete on the points involved, and there remained but one line of attack which was still open to us, viz, fritting the color at very high heats. Whether a stable red of good color can be produced at high temperatures, which will still remain good when dissolved in raw glazes fired at low temperature, under such conditions as prevail in roofing tile manufacture, I do not know.

Discussion By Ross C. Purdy,

Columbus, Ohio.

Notwithstanding the fact that the manufacture and use of chrome-tin pink has become very general among the potters, and that the formulae and directions for its preparation are given in many books, but little is known of its characteristics and peculiar behavior under varying conditions.

Most potters are very loth to give the slightest information as to how they make and use it, holding their information strictly secret. Very few investigators have published their results on this subject, and when they have, it has nearly always had reference to some minute detail, which alone would not give the reader much of an idea of the subject as a whole. Thus, it is with great interest that

potters and scientific investigators have read what Seger has given us, and later the paper of Hull in Vol. IV of these Transactions. Much valuable information has been published by these two writers, and it is hoped that these publications are but the beginning of a more general discussion on the subject. There surely cannot be any good reason to keep secret data, which, if collected, would undoubetedly result in making clear the exact conditions which govern the most successful manufacture of this useful but comparatively little understood color phenomenon.

The purpose of this note is not to describe any series of experiments made on chrome-tin pink glazes, but to discuss the results of Hull's investigations in the light of my own experience.

Adopting Hull's scheme of approaching the subject, the question of the most favorable composition for the pink frit will receive first attention.

His series were well planned to show the effect of varying amounts of the ingredients on the resultant color stain. Lack of time was undoubtedly the reason why various compounds of lime and chromium were not experimented with, but they should be before such sweeping conclusions as he made, were drawn. For instance, if fluorspar or gypsum were tried as sources of lime or potassium bichromate, lead chromate or chromium sesqui-oxide as sources of the chromium, he would have found a marked contradiction to some of the results as obtained with the ingredients he used.

In the first place he did not approach practical working conditions when he used chromic acid, for potters so far as I know, never use it. Its end reaction on the other ingredients cannot be the same as other chrome compounds are. It is analogous to the proposition of using potassium carbonate in place of feldspar, in any given formula.

It may be argued that the chromic acid would reduce very readily to chromic sesquioxide, and would thus act as when added as such with the advantage of a more thorough distribution throughout the mass of stain. Is the effect of

SiO_2 in a body the same whether added as quartz or soluble silicic acid? [1]

Then again he stepped beyond practical limits when he calcined his "pink frit" at cone 16. Certainly he can obtain pink frits at such a heat, as his own work proves, but that does not justify him in drawing the conclusion that "it is evident that a high temperature is necessary for the development of a frit which will produce a pink color in a glaze."

The writer has made good chrome pink stains or frits both at cone 8 and cone 4, but the *best* were calcined at cone 4. Heats higher than these are obtained in but comparatively few potteries where chrome-tin pink is produced to any extent, yet they are meeting with good success.

From what he writes, it would be inferred that he calcined his pink stain but once. It is the general experience that recalcination, after having washed and re-ground, produces the best results; hence, it is the general practice now to re-calcine the stain.

In choosing his best composition for a chrome-tin pink stain be takes into account the following consideration: [2]

"The tin might be raised without detriment to the frit itself, but it is not considered desirable to introduce more tin than is necessary into soft fire glazes. It may be that the tin could be decreased, but the results of these experiments do not indicate that this could be done to any considerable extent."

To compare my results with Hull's, five of the best stains (frits) which were calcined at cone 4 in 48 hours are tabulated on page 252.

The per cent. of SnO_2 in Hull's No. 15 stain, Series A-III is 52.3+ and of No. 16, 47.3 per cent. The average of these two stains agrees in the percentage amount of SnO_2 with those found in the table on page 252.

His statements as to the limits of variation in the amount of SnO_2 best to use in a stain are very true. Neither his nor my results would indicate that the tin could be decreased to any considerable extent. And if 50 per cent. SnO_2 will

1 Transactions Am. Ceramic Society, Vol. III, page 25.
2 Ibid, Vol. IV, page 236.

Chrome-Tin Pink Formulae.

No.	Per Cent.	Chem. Formula with RO as Unity.					Chem. Formula with SnO_2 as Unity.					Results in a Standard Glaze.
	SnO_2	RO	SnO_2	Cr_2O_3	SiO_2	B_2O_3	RO	SnO_2	Cr_2O_3	SiO_2	B_2O_3	
1	55.56	1.0	1.240	0 038	1.110	0.078	.0315 Na_2O .0306 K_2O .7444 CaO .8065	1.0	0.0306	0.893	0.03	Brownish, hard to disseminate in glaze
2	50.31	1.0	1.111	0.009	1.104	.....	.8825 CaO .0173 PbO .8998	1.0	0.0086	0.992	. ....	Good Maroon.
3	50.2	1.0	1.127	0.013	1.104	0.009	.0084 Kn_2O .8638 CaO .0149 PbO .8871	1.0	0.0115	0.9795	0.0084	Dark Maroon.
4	50.5	1.0	0.744	0.016	0.325	.....	1.1252 CaO .2187 Na_2O 1.3439	1.0	0.0215	0.437	.....	Blood Red.
5	50.5	1.0	1.000	0.066	0.978	0.008	.0040 K_2O .0041 Na_2O .8634 CaO .1284 PbO .9999	1.0	0.066	0.9787	0.0083	Pink.

suffice, of course it is not desirable to introduce more. But it is not desirable principally for the economic reason, and not because it is objectionable in a soft-fire glaze.

In his fourth consideration, he justifies Seger's use of more tin, because his stain was intended for higher fire glaze; and assumes that amount of tin would be detrimental to a soft-fire glaze.

What is the office of tin in a glaze, and does it enter into the glaze composition chemically, so as to materially alter its pyro-chemical behavior?

S. Burt[1] proved in very pretty and unique experiments that tin is slightly soluble in silicates and seemed justified in concluding that the soft-fire glazes do take some tin into solution. But he proved also that but very little was dissolved or at least but little remained in solution. The bulk of the tin, even when only 0.02 equivalent was added to the glaze, remained undissolved.

Stover[2] gives a formula of a cone 12 glaze where .04 equivalent SnO_2 has not gone into solution.

We are safe then in concluding that not much tin goes into solution whether added raw, and in a frit, or in a stain, at a high or low heat.

The question then is how much tin can we add without detriment to a soft fire glaze? I do not know. I have used 0.2 equivalent SnO_2 for ordinary fritted white enamel of practically the same composition as the red glaze, and made to fire on the same ware. I have never used a chrome-tin glaze having over 0.18 equivalent SnO_2, and have used successfully as low as 0.075 equivalent SnO_2, the best success being one with only 0.10 equivalent SnO_2.

The question of the use of more or less tin in a stain is not, then, one of its adaptability to a soft or hard fire glaze, but rather one of necessity and economy.

For example, take stain four in the above table; 0.1 equivalent (SnO_2-unity) gave a very deep red with good body to the color. With double that quantity, I did not get a desirable color effect, but the glaze was not impaired. Now,

1 Trans. American Ceramic Society, Vol. IV, page 139.
2 Trans. American Ceramic Society, Vol. IV, page 144.

if there is sufficient tin in that stain to produce the desired color and covering power by the use of only 0.1 equivalent, it does no seem necessary to use more.

From Burt's experiments before quoted, we learn then, that the office of SnO_2 is not that of a flux or acid, for it does not go into combination with the glaze, but that it remains inert and suspended. Therefore, if the stain is a stannate, as some suppose, it would not go into solution, and, as the above illustration shows, the pyro-chemical behavior of the glazes would not be materially affected as Hull supposed, when he says on page 243 "Naturally more flux was required to produce a mature glaze than would be necessary if less of the pink frits were used."

His second consideration was "Series A-I indicates that the chromic oxids (0.0375) is as high as is allowable."

Stain No. 5 above given has 0.066, and yet it was not green and the color effect in the glaze was a good red. Therefore, the use of more than 0.0375 Cr_2O_3 is *allowable*, but *not always justifiable.*

His third consideration "The lime was purposely made as high as Series A-III would warrant," leaves no basis for criticism, for he affirms nothing except what his trials would warrant. But, it will be noticed that my stain No. 4 contains 1.125 CaO which is 0.125 more than Hull's trials would warrant.

His further trials, Vol. IV, page 252, also show as he says in his conclusion "that a wide range in the quantity of lime used in the frit is allowable."

These differences in results between Hull's and my investigations are due principally to the fact that I used various compounds of lime and chromium and burned the frit or stain at a lower heat.

There is only one criticism to be made on the glaze series and that involves a very essential point. In every case, except in Series B, where the effect from increasing the content of boracic acid in a glaze was sought, the boracic acid was added *at the expense of* the silica. It is the experience of every glaze maker with whom I have discussed this point, that the silica should be as high as possible, for

it has a beneficial effect on the chrome-tin color. Therefore, while he was increasing a factor which he knew was detrimental, he was doing so at the expense of another factor which was beneficial. This accounts in a great measure for the fact that his most favorable combination of lead and boracic acid as described on page 251, Vol. IV, does not accord with the writer's experience.

The ratio of lime to the alkalies is also of decided importance. The highest proportion he used was 2 : 1, while it is the writer's experience that about 3 : 1 is the best ratio. By the use of a larger ratio, some of the lime can be added as carbonate, which the writer has found desirable for the better maturity of the glaze in general, and, in this case, owing to the increased lime, to this color in particular.

After considerable experimenting, the writer found that the glaze best suited for the production of chrome-tin pinks and reds was:

$$\left.\begin{matrix} 0.22\ PbO \\ 0.59\ CaO \\ 0.19\ KNaO \end{matrix}\right\} \left\{\begin{matrix} 0.16\ Al_2O_3 \\ 0.X\ SnO_2 \\ 0.Y\ Cr_2O_3 \end{matrix}\right\} \left\{\begin{matrix} 2.10\ SiO_2 \\ 0.475\ B_2O_3 \end{matrix}\right.$$

If the ordinates and abscissae of the lead and boracic acid were plotted on Hull's diagram given on page 251, Vol. IV, it would be found that the above glaze is more than 0.1 equivalent B_2O_3 within the area in which he says good results are improbable, and more than 0.175 equivalent beyond the limits within which he obtained his best results.

A METHOD FOR MAKING ENAMELED BRICK.

BY

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In 1900 the value of the enameled brick output of the United States was $323,630.00 while in 1901 it had increased to $463,709.00, a gain of about 43 per cent. That this increase was not even greater can be attributed to the comparatively high price of this product, for enameled brick have of late come into greater command in building construction. For use in wainscotings and wall surfaces in depots, hotels, or in any public building, or passage way; in dairies, bathhouses, power stations, etc., where cleanliness is desired; in elevator shafts, subways, etc., where reflected light is needed; or in any construction requiring an ornamental, smooth, bright, sanitary surface, the enameled clay surface has no satisfactory substitute. And of course for such uses the white enameled brick is almost invariably used and white is usually understood when reference is made to simply "enameled brick." There is a limited demand for colors for interior use, as borders or in oriental work or hearths, but the bulk of a manufacturers output is ordinarily white.

A great many enameled brick have in the past been imported from England, our own supply of first-class product being inadequate to the demand. In the past few years, however, a number of American manufacturers have offered the market very creditable ware. Yet, while the ware is first-class, the high price of enameled brick undoubtedly prevents their specification in many instances where their use is strongly desired.

Two years ago it was the writer's good fortune to be assigned the task of producing a white enameled brick which would be of good quality but moderate in price. The experiments made to accomplish this end brought out many

interesting points while leading to very satisfactory results. Believing that the mode of procedure in the work as well as the results attained and incidental facts brought out may be of interest and possibly of value to the members of this society it will be the purpose of this paper to trace the work from beginning to end.

THE BODY:

The enamel was to be applied to the following fire-clay. It is known as the Lower Mercer clay, occurring in a vein from six to twelve feet thick, and won by mining. An analysis of this clay gave:

SiO_2	Free	24.20
	Combined	34.66
Al_2O_3		27.96
Fe_2O_3		1.40
CaO		0.51
MgO		0.64
Alkalies		2.73
Combined water		8.82
		100.92

This clay burned to a hard, dense, body, light buff in color, at cone 8. The question as to whether to apply the enamel to the green or to burned ware naturally was amongst the first to arise. To coat dry-press brick in the green state with a glaze or enamel is a delicate process entailing much loss and a poor quality of product. As the product of the plant was almost exclusively dry-press brick the making of mud brick for the reception of an enamel would have required much new machinery. These considerations swung the choice towards a two-fire product and the fact that in the course of burning there were always more or less soft-burned brick which were unsalable except as culls, led to the decision to use these soft-burned brick as biscuit for the enamel. To use at the start bricks which would not sell as builders, merely because not hard enough, seemed the first step towards securing a moderate-priced enameled brick. Of course, the supply of these soft brick was limited but would prove ample for a start and for small

sales. It would not be necessary to make a special biscuit burn except in case of a much larger run on enameled brick than was at that time in sight. Furthermore, upon consideration of the care, time and loss in enameling green ware and burning in one fire, it was estimated that the difference in the cost of burning would be off-set by the ease and rapidity of handling, and small loss attendant upon a two-fire product.

The soft burned bricks to be used as biscuit had shrunk on the average, in volume, 8.2 per cent of the die measure. The hard burned bricks of the same clay usually shrunk 13.4 per cent, so that the body used had received about 61.2 per cent, of its total shrinkage. The bricks were soft and punky and of course very porous.

THE GLAZE.

White enameled brick are made either by applying a true enamel (usually tin) to the body or by using a clear, transparent glaze over a white engobe which completely conceals the true body color. As a tin enamel requires a calcareous clay for the best results, and as the clay to be used was a fire-clay with but little lime, it was decided the engobe-glaze method would offer fewer difficulties and better ware.

To insure durability, enameled brick must have a hard-burned body and an enamel which has been burned fast to the body, is well matured and is free from crazing or shivering. When used in light shafts or in other outside work, severe weather changes soon destroy a poorly enameled surface. The chance of water entering the wall and consequent freezing and thawing breaking off the enamel must be made practically impossible.

In view of these requirements, a glaze of the porcelain type was selected as desirable, to mature at the point where the body became very hard and dense, *i. e.* cone 8. The porcelain glazes are very durable and not as prone to craze as lower fire glazes.

Using the formula of Seger cone 4 as a starting point a series of glazes was made the extremes of which it was

certain would be too soft and too hard respectively for this heat.

This series was as follows:

SERIES I.

No.	K_2O	CaO	PbO	Al_2O_3	SiO_2
1	0.3	0.4	0.3	0.5	4.00
2	0.3	0.5	0.2	0.5	4.00
3	0.3	0.6	0.1	0.5	4.00
4	0.3	0.7	0.0	0.5	4.00
5	0.3	0.7	0.0	0.6	4.80
6	0.3	0.7	0.0	0.7	5.60

The use of lead above the temperature which will turn cone number 1 is not recommended by Seger. The writer, however, has used lead with fair success at cone number 3 and had heard of its use in porcelain glazes, the idea being that even if the lead did volatilize, it would start good fusion before going. Since making these experiments the writer has actually observed in a large plant the use of lead in a porcelain glaze fired at cone 8–9†. With not much faith however, that lead could be used at this temperature to advantage, it was decided to try it in order to locate the type of glaze needed by showing a lead glaze not feasible. The glazes numbers 5 and 6 it was almost certain would be too hard.

The glazes were made up in about three pound batches, ground in a small jar mill with flint pebbles, put through a 120 mesh sieve and excess water siphoned off until a Baume' hydrometer dropped into the slip gave a reading of 40, this thickness having been found to work well on the soft body. Soft burned buff brick were dipped with the glaze and burned in saggers at cone number 8 in large down-draft kilns, amongst other ware.

†This glaze, while bright, smooth and clear is subject to crazing.

The results of the test of this series were as follows:

No.	Condition of Fired Glaze.
1	Thin—Brick dry in places—Crazed.
2	Thin—Brick dry in places—Crazed.
3	Thin—Crazed.
4	Crazed slightly—Not entirely clear—Smooth and fairly bright.
5	Milky—Not melted to clearness.
6	Milky—Not as clear as No. 5.

From the foregoing it is evident that a glaze of the type of number 4 was needed but one that should be somewhat softer.

Seger* has shown that cone number 4 is the most fusible glaze of the porcelain type. To secure greater fusibility therefore, other ingredients must be introduced than those indicated in the cone number 4 formula.

A complexity of bases, using magnesia and zinc, was next tried, keeping the alumina and silica constant. The series was as follows:

SERIES II.

No.	K_2O	CaO	MgO	ZnO	Al_2O_3	SiO_2
7	0.3	0.6	0.1	....	0.5	4.00
8	0.3	0.5	0.2	....	0.5	4.00
9	0.3	0.4	0.3	....	0.5	4.00
10	0.3	0.3	0.4	....	0.5	4.00
11	0.3	0.4	0.25	0.05	0.5	4.00
12	0.3	0.4	0.2	0.10	0.5	4.00
13	0.3	0.6	0.0	0.10	0.5	4.00

The glazes were treated the same as those in Series I and applied to buff bricks and burned in large kilns to cone number 8 with the following results:

No.	Condition of Fired Glaze
7	Milky.
8	Milky—Not as fusible as No. 7. } All far from
9	Milky—Not as fusible as No. 8. } being well
10	Milky—Not as fusible as No. 9. } matured.
11	Cloudy—But better than any of the above.
12	Cloudy—But better than No. 11—Smooth, glossy.
13	Almost clear—Smooth and bright.

*Translations of Seger's Collected Writings Vol. I, Pg. 241.

From this series it is clearly seen that magnesia is a harder flux than lime and if used to replace the latter the glaze is hardened thereby. This bears out Seger's statement as to the order of fluxes. The replacement of a little magnesia by zinc gave a correspondingly small improvement. The dropping of magnesia entirely and the substitution of 0.1 equivalent of zinc oxide for 0.1 equivalent of calcium oxide in glaze No. 13 immediately gave a glaze far superior to any of the lime-magnesia glazes, and also better than the lime-potash glaze, No. 4, indicating that zinc has greater fluxing power than lime or magnesia, or than a combination of these.

The failure of a complexity of bases in this series to give more fusible glazes does not harmonize with Cannan's* results with raw lead glazes, nor with his conclusions with regard to the fluxing power of magnesia. Where Cannan, working at a temperature of cone 04-02, secured better glazes the greater the number of oxides he used to make up his RO, and with magnesia obtained a higher single replacement of PbO than with any other oxide, the writer, at cone 6-8 finds a complexity of bases, using magnesia, very unsatisfactory, and that any replacement of CaO by MgO in a porcelain type glaze at once hardens the glaze.

Glaze No. 13 being the clearest and brightest glaze so far, developed, but this still being a trifle hard, it was decided to next run a series of lime-zinc glazes and also to try replacing zinc with barium.

This was done as follows:

SERIES III.

No.	K_2O	CaO	ZnO	BaO	Al_2O_3	SiO_2
14	0.3	0.65	0.05	....	0.5	4.00
15	0.3	0.65	0.05	....	0.5	3.80
16	0.3	0.65	0.05	....	0.5	3.50
17	0.3	0.60	0.10	....	0.4	4.00
18	9.3	0.60	0.10	....	0.4	3.80
19	0.3	0.65	....	0.05	0.5	4.00
20	0.3	0.60	....	0.10	0.5	4.00
21	0.3	0.60	....	0.10	0.4	4.00

*Trans. Am. Cer. Soc. Vol. III, 126.

The results of this test are shown below:

14, 15, 16, 17, 18 — All were smooth, bright glazes but No. 18 showed best maturity, the others holding more or less bubbles in suspension. No. 18 was slightly crazed in corners.

19, 20, 21 — Not noticeably different in appearance from the corresponding zinc glazes but all were badly crazed.

Number 18 being almost entirely satisfactory, the flint was increased to rid the glaze of crazing. It was found that this was accomplished by a very small addition, and the glaze finally accepted as being suitable for the work had the formula:

$$22\left\{\begin{matrix}0.3\ K_2O\\0.6\ CaO\\0.1\ ZnO\\\hline 1.0\ RO\end{matrix}\right\}\ 0.4\ Al_2O_3\ \left\{\ 3.825\ SiO_2\right.$$

The foregoing experiments with magnesia resulting so differently from Cannan's, another trial was made to verify the previous work. This time magnesia was used to replace lime in glaze No. 22, a glaze known to work well at this temperature. The introduction of burned, slaked and bolted dolomitic limestone was also attempted as a source of lime and magnesia.

To this end the glazes were made up replacing first 0.2 and then 0.3 equivalents of the lime in glaze No. 22 with magnesia, as follows:

No.	K_2O	CaO	MgO	ZnO	Al_2O_3	SiO_2
23	0.3	0.4	0.2	0.1	0.4	3.825
24	0.3	0.3	0.3	0.1	0.4	3.825

Furthermore, dolomitic limestone, prepared as noted above and secured from the same dealers as furnished Cannan's supply, was used in two glazes. In one glaze, the 0.6 equivalents of CaO called for in glaze No. 22 was replaced by 0.6 equivalents of limestone, while in the other the amount of whiting called for in the batch receipt of No. 22 glaze was

replaced pound for pound by dolomitic limestone. The limestone in question, after burning, gave on analysis*:—

$$.51\ Ca(OH)_2$$
$$.49\ Mg(OH)_2$$
$$1.00$$

Thus the limestone glazes were composed as follows:

No.	K_2O	Limestone.		ZnO	Al_2O_3	SiO_2
		CaO	MgO			
25	0.300	0.306	0.294	0.100	0.400	3.825
26	0.228	0.354	0.341	0.076	0.305	2.982

Glazes Nos. 23, 24, 25 and 26 were now applied to light buff bricks in the usual way and trials placed at the top, middle and bottom of a small down-draft kiln set with enameled brick. The kiln was burned off at the usual temperature, cone 8 in the top and cone 6 in the bottom. On cooling and drawing the kiln, the results of the test were found to be as shown below:

Glaze No.	Top of Kiln.	Middle of Kiln.	Bottom of Kiln.
23	Melted to smoothness but dull, milky and full of bubbles. Far from good fusion.	About same as top.	Very imperfectly fused. Dull and milky.
24	Very cloudy and imperfectly fused. Similar to No. 23.	About same as top.	Barely smooth. Some of the trials not fused sufficiently to give smooth surface.
25	Fairly smooth and glossy but very poor fusion—glaze cloudy thoughout.	About same as top.	Poor fusion—rough and no gloss—not much more than a sintered mass.
26	Not as good as No. 25.	Mostly rough and not fused at all except a few near bag.	Not as good as No. 25.

In addition to securing the desired glaze for the work in

*Trans. Am. Cer. Soc. Vol. III, 127.

hand, the above experiments brought out the following facts:—

(a.) Neither magnesia nor dolomitic limestone offer any encouragement for their use as fluxes in a glaze of this type and maturing temperature.

(b.) Magnesia is below lime in value as a fluxing agent at this temperature.

(c.) Zinc has greater fluxing power than lime.

(d.) That barium has at least equal fluxing power with zinc but gives rise to crazing if substituted for zinc in a zinc-lime glaze free from crazing.

THE ENGOBE.

Having perfected a satisfactory clear glaze, as given in No. 22, the next step was to secure a white engobe to apply between the body and glaze The engobe must be white, burn reasonably hard at the temperature used and shrink just enough to neither shell off, nor crack nor curl up.

Langenbeck* cites the case of a pure china clay being used as an engobe for enameled brick burned in single fire at cone 9-10. At the temperature at which it was desired to fire, however, a china clay in this case would be too soft and shrink to much for the body shrinkage. To reduce the shrinkage, flint is the best agent while for hardening the engobe feldspar is most suitable. With these three materials therefore, a series of engobes was made up varying the proportions as follows:

No.	China Clay.	Flint.	Feldspar.	Formula.		
				K_2O	Al_2O_3	SiO_2
1	75.00	0.00	25.00	.135	1.00	2.55
2	75.00	15.00	10.00	.058	1.00	3.03
3	60.00	25.00	15.00	.104	1.00	4.02
4	50.00	30.00	20.00	.156	1.00	4.80

The slips were blunged by hand, put through a 40 mesh sieve, and then through a 100 mesh sieve. By experiment it was found that the best working thickness was

*Chemistry of Pottery—Pg 144.

Baume 45°. On coating a number of bricks with the above engobes and burning, the following results were noted:

No. 1 had cracked slightly.

No. 2 was soft.

Nos. 3 and 4 were both good, but No. 4 was harder and hence preferable.

No. 4 was the engobe chosen for use.

In a paper entitled "Stoneware Slips or Engobes" Geijsbeek† speaks of obtaining results by substituting one clay for another in an engobe mixture. This seems a long way to take to get the proper engobe. After one trial of 25 per cent flint and 75 per cent china clay, Geijsbeek gives up flint and says "as it seemed strange that flint could not be used so far in an engobe. I have started experiments on that subject, but as yet I have been unable to finish same or to come to any conclusion." That he will find flint a valuable agent in engobe compounding, I do not doubt at all. Using one clay, and with flint and feldspar as controlling agents for shrinkage and hardness, a wide range of engobes can be made, and this seems a more exact method than to shift clays.

In order to increase the tenacity with which the engobe holds to the body, five per cent. of sodium carbonate was used in the engobe, being added as a solution, in the least possible amount of water, after the engobe had been made up to the proper thickness. This expedient is the practice among stoneware men to prevent crawling of engobes and glazes, borax and calcium sulphate being also used for the same purpose.

On making a trial of No. 4 engobe with No. 22 glaze, a very white, smooth and bright enamel was obtained.

While experimenting with engobes, a few colors were attempted as follows:

A blue frit was made up corresponding to the formula

$$\left.\begin{matrix}0.50\ Na_2O \\ 0.50\ CoO\end{matrix}\right\} 2.00\ SiO_2$$

and melted in flint-lined crucibles in a blacksmith's forge. The resulting glass, which was a very intense blue, was

†Trans. Am. Cer. Soc. Vol. IV—48

ground to 120 mesh fineness in jar mills, the water dried off, and the powdered frit boxed for use. On adding a little of this blue frit to engobe No. 4, a very good blue engobe was obtained, which, covered with No. 22 glaze, gave a very acceptable blue enamel. Two shades were made as follows:

Blue No. 1 (Light)	97.5 parts engobe No. 4. 2.5 parts blue frit.
Blue No. 2 (Medium)	95.2 parts engobe No. 4. 4.8 parts blue frit.

Another method of securing a blue engobe was to add a cobalt solution direct to the engobe No. 4, the latter being sufficiently alkaline to precipitate the cobalt throughout the mass, and give a very uniform coloring in the resulting engobe. By adding 770 c. c. of a ten per cent. $CoCl_2$ solution to each one hundred pounds (dry weight) of engobe, a very delicate, pretty blue is obtained. This is equivalent to 0.10 per cent. CoO. When the cobalt solution is added the cobalt is precipitated as a carbonate, thus leaving sodium chloride where before we had sodium carbonate in solution in the engobe. This does not affect matters seriously, however, as the chloride is almost as efficient as the carbonate as a fastening or binding agent. At any rate, the colored engobes adhere to the body as tenaciously as the white engobe. Neither white or colored engobes at any time gave trouble from crawling.

This process of precipitation does away with fritting and as cobalt chloride is no more expensive than a good grade of the oxide, the process is also much cheaper. Iron colors also can be obtained by the precipitation method.

A very good chrome-green was obtained by adding raw chromic oxide to No. 4 engobe, in the proportion of thirteen per cent. oxide to eighty-seven per cent. engobe. This gave a rather dark sage-green enamel. Other shades were not attempted, as colored enamels were not considered of sufficient importance.

A very satisfactory pink engobe was made by using a pink stain or frit, made in accordance with Seger's formula, to the amount of eight or ten per cent. in the white engobe.

In attempting to use copper for sea-green effects, the color was obtained successfully except around the edges of

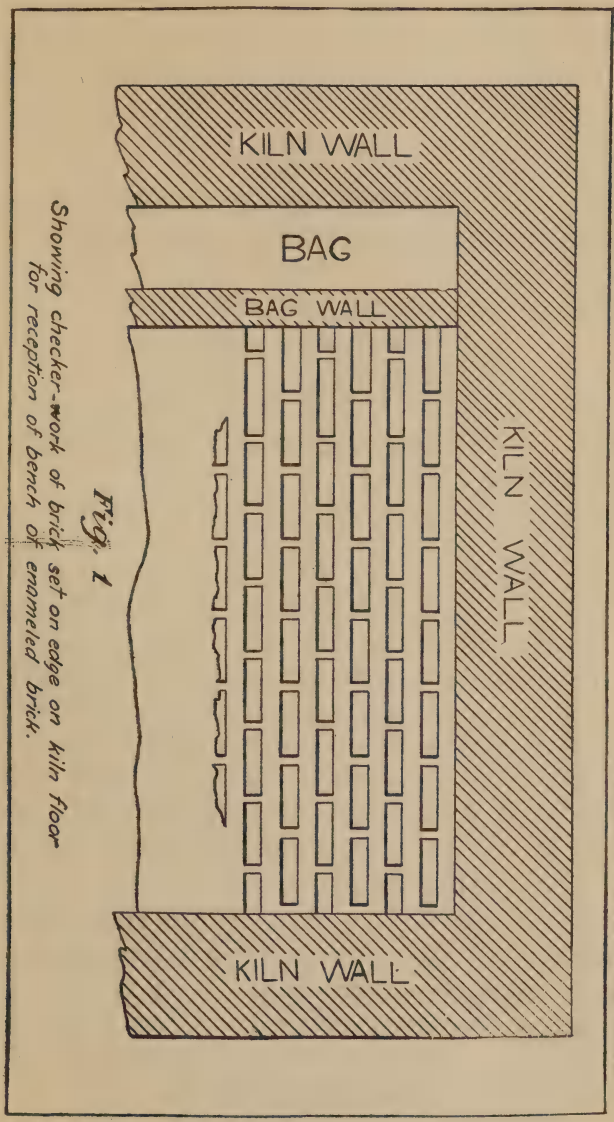


Fig. 1

Showing checker-work of brick set on edge on kiln floor for reception of bench of enameled brick.

the brick, where the copper volatized leaving a white edging entirely around the enameled face. This defect was sufficient to bar out copper-greens. On breaking a brick coated with copper-green enamel, it was noticed that the color had left the engobe entirely, and what really existed was a *green glass over a white engobe.* The copper had evidently tried hard to get away, but the heat and duration of burn were not sufficient to expel it entirely.

A fairly good brown engobe was obtained by the use of 12 parts of commercial manganese to 88 parts of white engobe.

This manganese gave an analysis:

MnO_2	81.01
Fe_2O_3	5.73
Silicious residue	13.26
	100.00

Uranium colors were a failure, coming out a dirty green in every one of several tests.

All colors were obtained by making the colored engobe and then treating and applying to the ware just as was done with the white engobe. Special attention had to be paid to location of colors in the kiln however, as will be noted later.

In general, it may be said, that having secured a satisfactory white engobe, colored engobes may be easily obtained by the introduction of coloring oxides or colored frits. The small proportion of the coloring agent usually required produces no physical defects in the engobe. A good white engobe will stand in some cases fifteen per cent. of a coloring oxide, and still burn as smooth and perfect as originally.

USE OF A GREY BODY.

An attempt was made to use the white enamel as above developed on light grey brick, in order to increase the available biscuit supply, but on trial it was found that the manganese in the grey body was sufficient to color the engobe and darken the glaze to such an extent as to make the product unsalable as a good white enameled brick.

DIPPING AND CLEANING.

The glaze and engobe had now been developed in an experimental way, and the process of making the brick on a

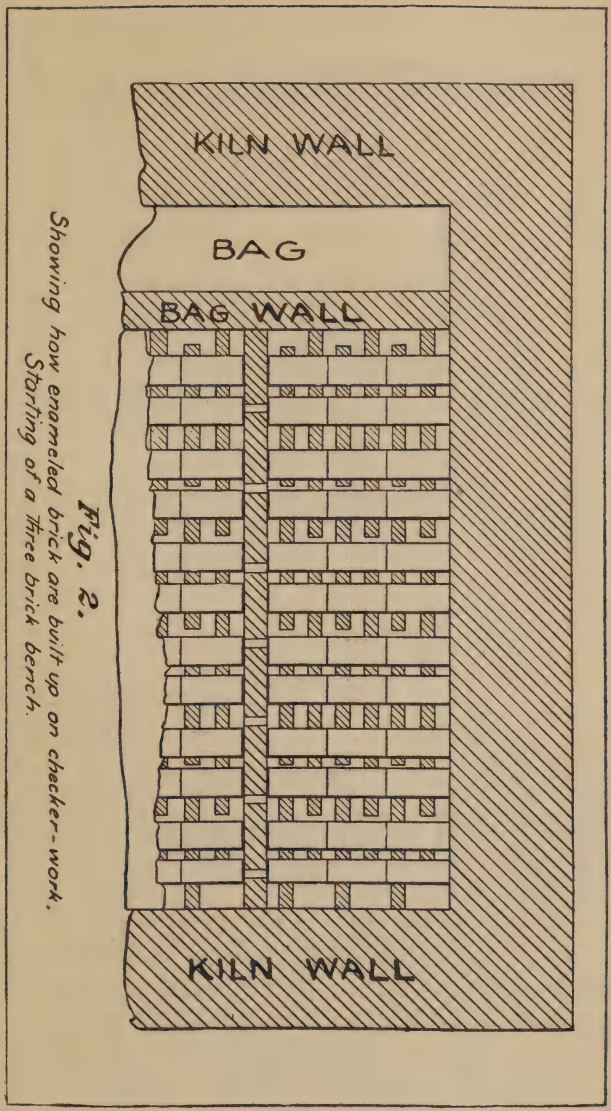
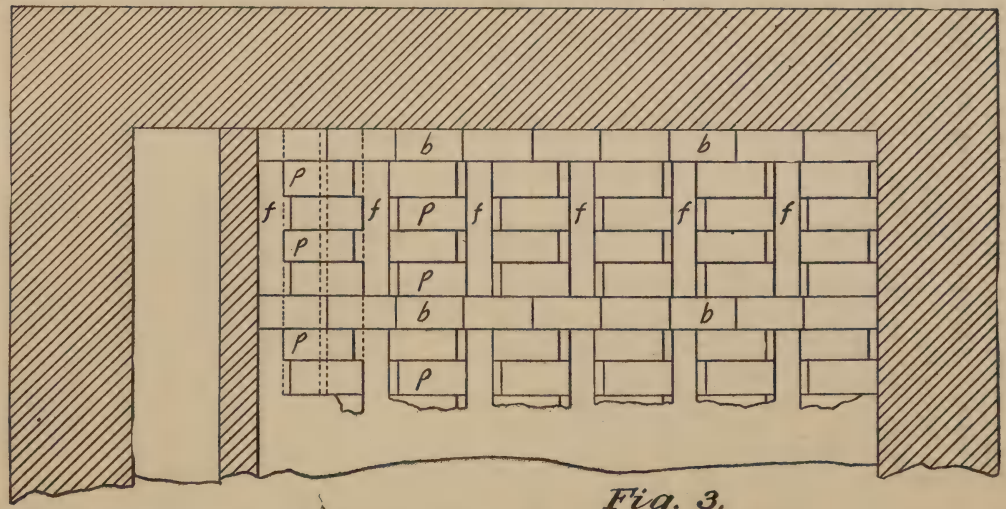


Fig. 2.

Showing how enameled brick are built up on checker-work. Starting of a three brick bench.

manufacturing scale was taken up as the next step. The experiments for a white enamel had scarcely been completed, when an order was received for 35,000 white enameled brick for a light-shaft in an office building. The brick made by the following method, therefore, were for an actual order and every effort was made to devise a rapid and economical method.

Soft-burned light buff brick were set apart by the kiln drawers and sent to the enameling room, a small brick building which had formerly been used as an oil storage house, but was left vacant when the use of oil as a fuel was discontinued. Here the brick were laid face up on a long bench, and subjected first to the cleaning process, consisting of going over the face to be enameled with an iron scraper to remove adhering sand, and then with a stiff brush to take off all further dirt or dust. This required but little time. Two men could easily go over 100 brick a minute. The bricks were then dipped into the engobe two at a time, the dipper holding one in each hand. One man dipped into the engobe and about twenty brick behind him came the glaze dipper who had helped with the engobe until the two operations were sufficiently spaced. By experiment it was found that by working with the engobe at a thickness of 45° and the glaze at a thickness of 50° (Baume) and dipping into the glaze a few moments after the application of the engobe, a very smooth uniform coat resulted, free from pin-holes or bubbles. Both glaze and engobe were prepared as in the preliminary experimental work. The glaze and engobe were both occasionally stirred up by means of wooden paddles kept near the dipping tubs. Following the glaze dipper as close as he could conveniently work, came the cleaner who removed the excess engobe and glaze with a large spatula. With one stroke the excess coatings along one side could usually be nicely sliced off so that only a few strokes to each brick were required. By this means it was found the brick could be more easily, rapidly and effectually cleaned than by allowing the coatings to dry and then brushing off superfluous material as is the practice in many plants.



b - Binding course running clear across kiln.
p - Brick protecting enamel spaces. . . .
f - Flue spaces. . . . . .

Fig. 3.

Showing binding course for single bench.
Dotted lines indicate enameled brick below.

In dipping headers, quoins or shapes, such as bull-noses, octagons, etc.. the dipping process was necessarily slower, the brick being dipped one at a time and requiring more care to get the surface properly covered.

The dipped and cleaned brick were now removed from the bench to pallets holding eight brick each and removed to the storage shed just back of the dipping room.

SETTING AND BURNING.

Burning was accomplished in small rectangular down-draft kilns (designated on account of their size "baby kilns") having twin fire-boxes. At first saggers were used, the brick being stood on end, twelve in a sagger. In this way only 1500 brick could be set in each kiln; many saggers were broken from the great weight on them, and setting and drawing a kiln involved much labor. It was seen at once that this system was too expensive. A scheme was then devised of setting the brick without saggers, by building up the bricks so that the fire gases did not come in contact with the enameled surfaces. The method adopted was this: The brick were brought from the storage room on pallets, and set down on the kiln floor. The distance from the storage shed to kiln was only from ten to fifteen feet and one carrier could easily keep two setters supplied. The setters first set burned, unglazed bricks on edge on the kiln floor in rows running parallel to the kiln door and extending clear across the kiln, the rows being about 1½ or 2 feet apart. (See Fig. 1, p. 267). This was for the purpose primarily of allowing the kiln gases free play at the kiln bottom, and ready access to the flues, and secondarily to keep the enameled bricks from the floor, where they would come into contact with sand and ash. After a distance of three brick lengths from the rear kiln wall was reached, the enameled brick were then set on flat on this checker course and built up in walls running parallel to the fire bags. The first course above the checker work however, was usually set in burned, unglazed brick. The walls of enameled brick were so spaced that there was a narrow space and then a wider space alternating. The enameled faces of the brick formed

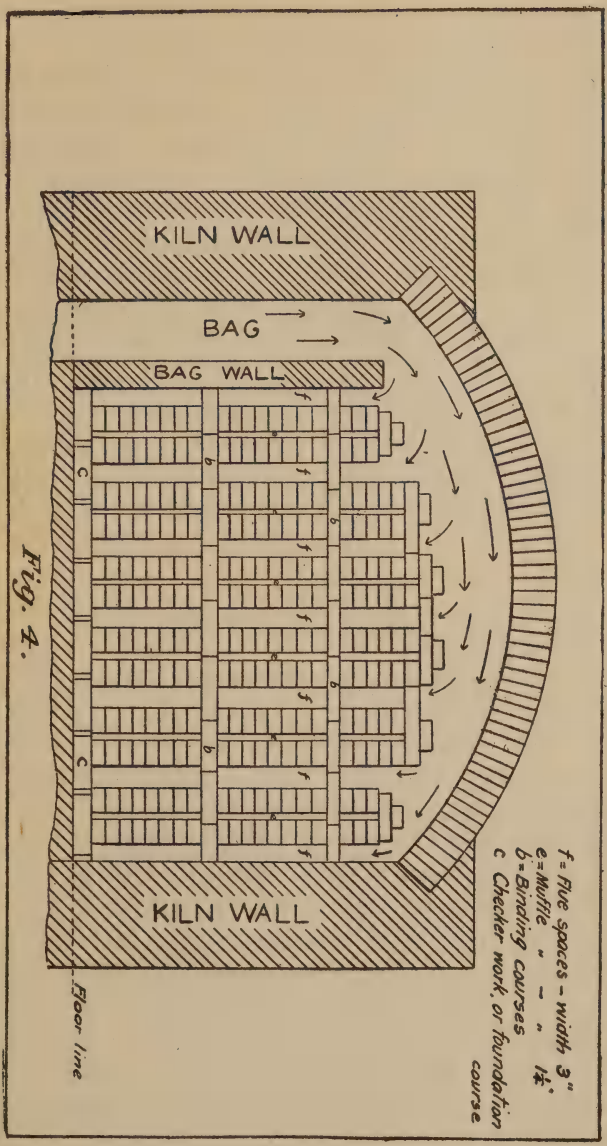

KILN WALL
BAG
BAG WALL
KILN WALL
Floor line
f = flue spaces - width 3"
e = Muffle " - " 1½"
b = Binding courses
c Checker work, or foundation course

Fig. 4.

the narrower spaces, and the backs of the brick formed the wider spaces, the latter constituting the flues through which the fire gases passed. (See Fig. 2, p. 269). When a height of eight bricks had been reached in the walls, a "binding" course of unenameled bricks was then set to hold the columns straight and prevent rolling. The narrow spaces on which the enameled faces fronted were covered completely, while the larger flue spaces were left open except at intervals where the true binding course ran clear across the kiln. In this way a muffle was built up to protect the enameled faces. (See Fig. 3, p. 271). As the top of the kiln was approached, the middle walls were built higher than the side walls to follow roughly the curve of the crown. When the top had been reached, a final binding and protecting course was put on as shown in figure 4 (see page 273).

The brick were built up in three brick benches.

In setting quoins, bull-noses or shapes, triple walls were used instead of the double wall arrangement, the middle wall being used for these shapes and being protected completely from the fire gases by the two side walls of ordinary enameled stretchers. (See Fig. 5).

To space the bricks, a wooden form termed by the setters a "goose-yoke" was used. This was simply a U-shaped wooden frame and was used in starting from each binding course.

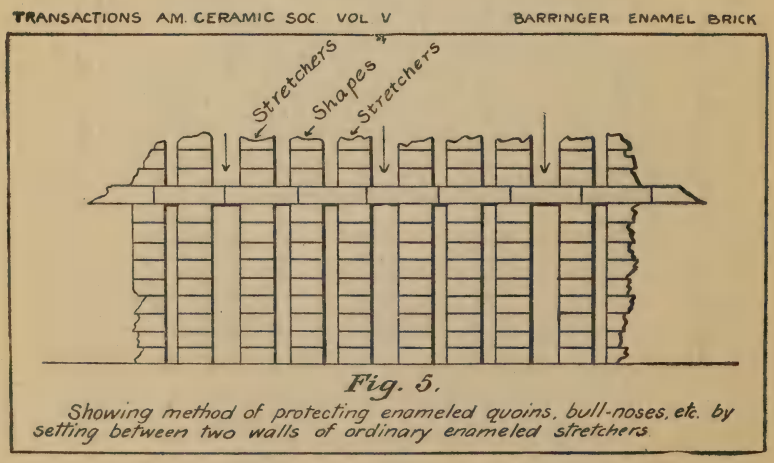


Fig. 5.

Showing method of protecting enameled quoins, bull-noses, etc. by setting between two walls of ordinary enameled stretchers.

FIG 6. THE DIPPING HOUSE AND KILNS.

FIG. 7. THE "BABY" KILNS.

By setting in this manner, the capacity of the kiln was increased to 3000, and the labor of setting and drawing was much reduced.

In setting, pyrometric cones were placed in convenient places at top and bottom of the kiln, numbers 6, 7 and 8 being used in the bottom, and 7, 8 and 9 in the top. Peep holes in each end of the kiln were made, so that the cones could be easily seen.

Three men could start in the morning, set a kiln of enameled brick in this fashion, build the wicket and have the fire started in the evening.

Burning usually required from 66 to 72 hours, divided into three periods:

(a.) Slow heating up by wood fires on the floors of all fire boxes, 12 hours.

(b.) Coal fires on bars in all furnaces; firing every hour for 12 hours in all fire boxes, then in alternate boxes every half hour for 12 hours, and finally every twenty minutes in alternate furnaces, carrying the heat up as fast as possible until cone 8 was turned slightly in the top, which usually required 24 hours of the twenty-minute firing.

(c.) Soaking or distribution stage. After cone 8 had been turned on top, which usually occurred before cone 6 in the bottom was affected, the heat was held as steady as possible by careful firing until a nearly uniform temperature was attained throughout the kiln. In the course of from six to twelve hours, cone 6 and often cone 7 would go over in the bottom while there had been no material change in the top. This was deemed the finishing point, and firing ceased. Cone 8 could not be turned in the bottom without overfiring the top.

The finishing point was determined solely with pyrometric cones. At first it was the practice to draw trials towards the close of the burn, but later the cones alone were relied upon, and never failed the purpose. If number 9 cone was melted down in the top, we knew what to expect from the top on drawing the kiln—blistered body and thinned glaze. If the proper cones were not melted in the bottom, dull-finish enamel could confidently be expected. On be-

coming acquainted with the merits of the cone by actual practice, the burners took to watching them carefully, and handled the kilns to get the cones down as uniformly as possible.

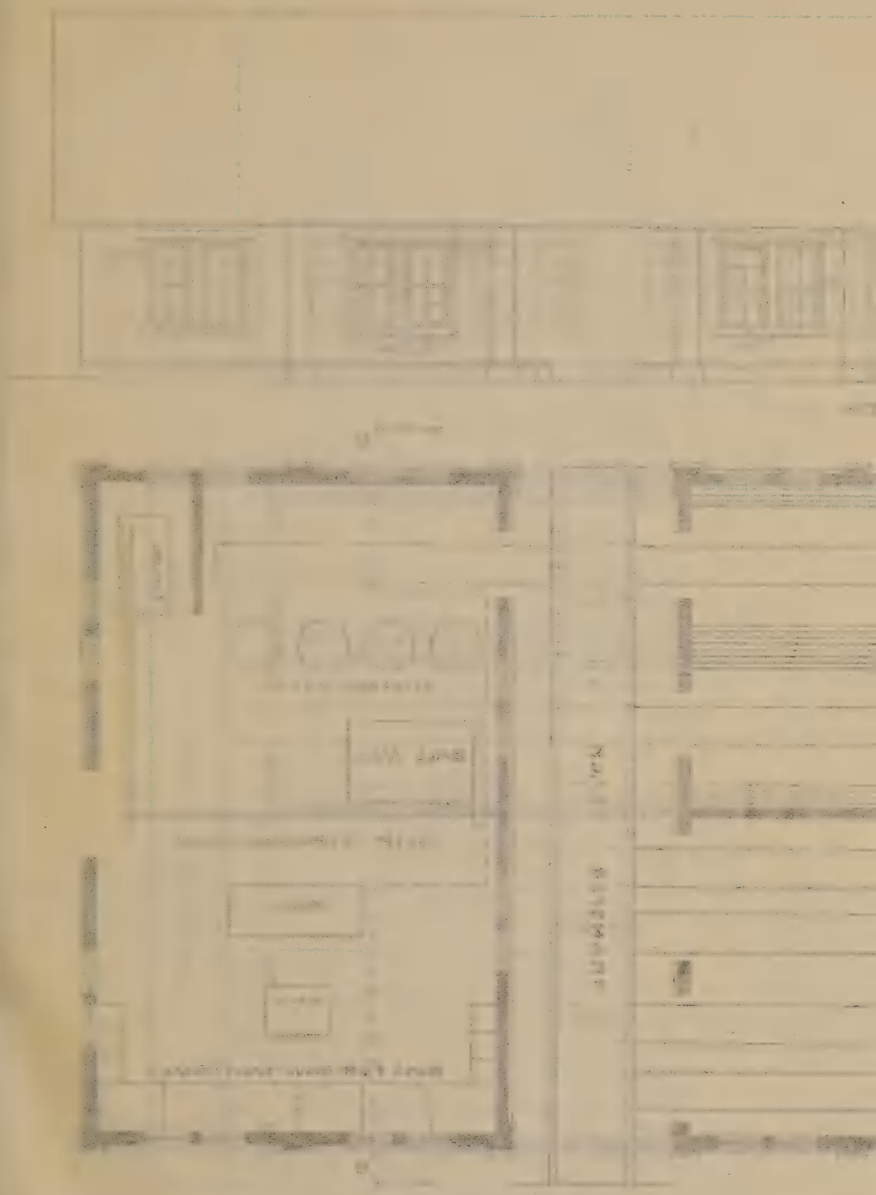
Reduction was not resorted to in burning, and oxidizing conditions prevailed throughout most of the burn.

Immediately after firing ceased, the dampers were shoved in and the holes in the kiln crown were uncovered. This took much of the heat from the kiln, without sending cold air in amongst the ware. After about twenty-four hours, dampers were pulled and fire doors opened. The wicket was pulled down after another twenty-four hours, and the kiln cooled as rapidly as possible, the drawing crew usually being able to take out the ware twenty-four hours after the wicket was down. At first, more rapid cooling was tried by leaving dampers out, tops off, and fire doors open immediately after firing ceased, but this resulted in "cooling checks", consisting of long straight cracks extending clear across the enameled face. The practice was gradually changed, therefore, to that above, which gave practically no cracked enamel.

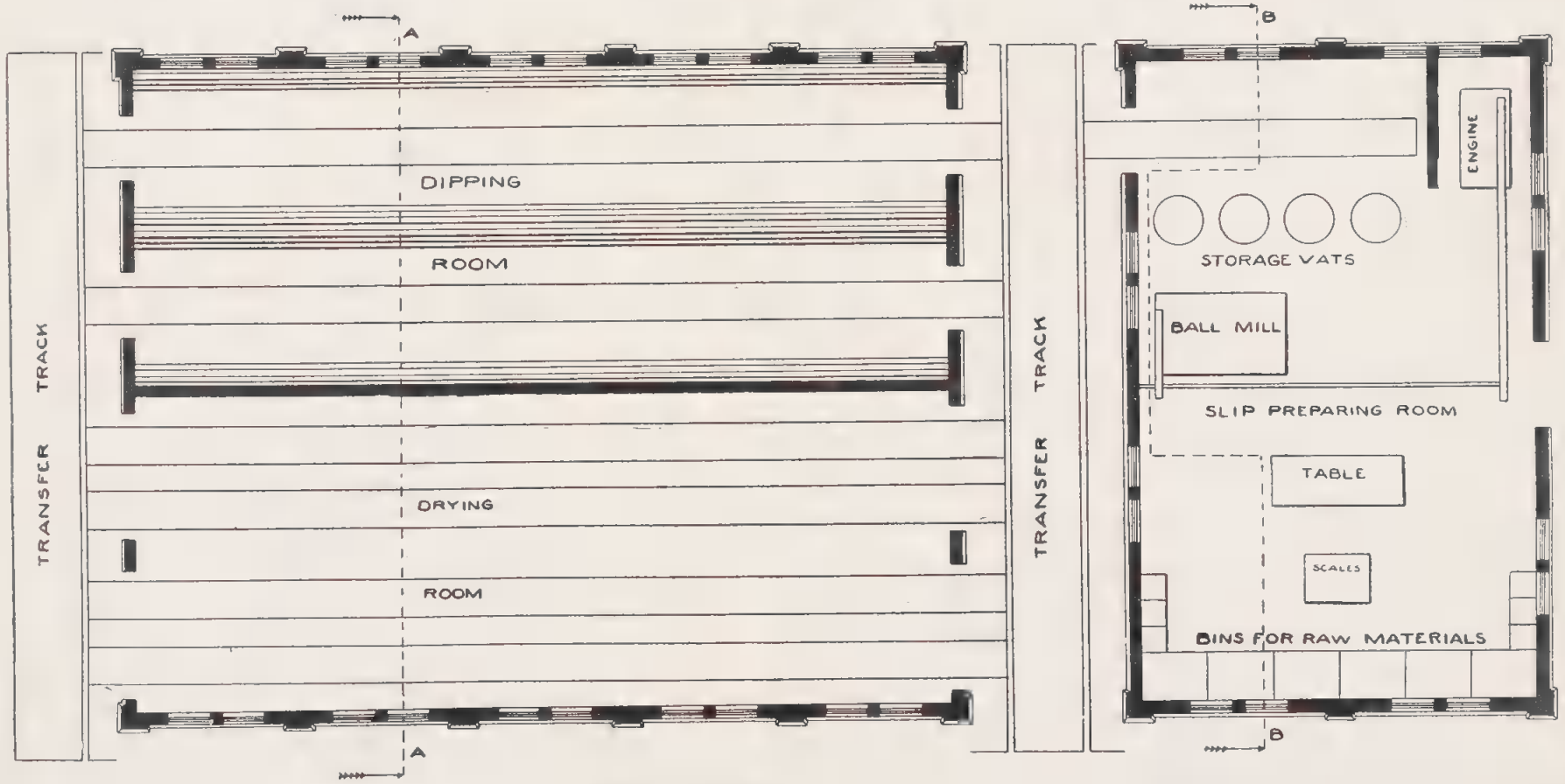
In burning colors it was found that blue and manganese iron brown were comparatively easy to burn. The coloring agents acted as fluxes, and fused partially into the glaze, giving a very uniform shade. In chrome green and chrome-tin pink, however, the glaze must be perfectly matured in itself to give a clear, bright color, as it receives no aid from the engobes colored with these agents. On breaking a brick enameled in green or pink, the line of contact between engobe and glaze was very sharply defined and the color had not fluxed into the glaze covering. It was always necessary for the best results therefore, to burn pink and chrome green in the hottest portion of the kiln, while the other colors could be placed in almost any section.

DRAWING, SORTING AND SHIPPING.

The kilns were drawn by running an ordinary brick car to the kiln, and loading on the enameled brick just as is done with face brick. Not much more care was used with the en-



SIDE ELEVATION



GROUND PLAN

PLANS FOR ENAMELED BRICK PLANT

DAILY CAPACITY 5000 STANDARD BRICK

SCALE

ameled brick than with unenameled brick. The cars were run to the stock sheds, and the brick sorted under ground glass sky-lights. The color was usually very uniform, and sorting resolved itself into merely removing defective brick, such as contained specks, cracks, broken corners or unusually rough edges. Only two sorts were recognized—"firsts" and "seconds". The "firsts" averaged 80 per cent.

In shipping, the bricks were packed in straw in cars, just as is the custom with face brick, with the exception that a little more straw was used in packing. The bricks were not wrapped in paper, or otherwise protected, and the shipment of a number of cars demonstrated the precautions against breakage to be ample.

TESTS AS TO DURABILITY.

Enameled brick made by the above process have undergone two winters in a large light shaft in an office building and are just as good now as when laid in the wall. This is not very long, it is true, but there is every reason to believe that they will stand the test of time. As a severe test, about twenty of these brick were laid to form the top courses in a stack of one of the "baby" kilns. In this position they were subjected to red heat at one time, and to freezing at another. The brick remained in this position all winter and upon examination in the spring following, showed no signs of cracking, whatever.

A CONVENIENT PLANT.

The work outlined above was accomplished without building a special plant, by using what room was available and rigging up apparatus as necessity demanded in the progress of the work. The small kilns were all that was built especially. Realizing, however, that the process could be cheapened by better facilities for handling the ware, a build- was planned in which there were three rooms:

(a.) A glaze and engobe preparing room.

(b.) A dipping room.

(c.) A drying room.

The arrangement of this plant is shown in the accompanying plates. There are two buildings under one roof, the

covered way between the buildings affording a good transfer in bad weather.

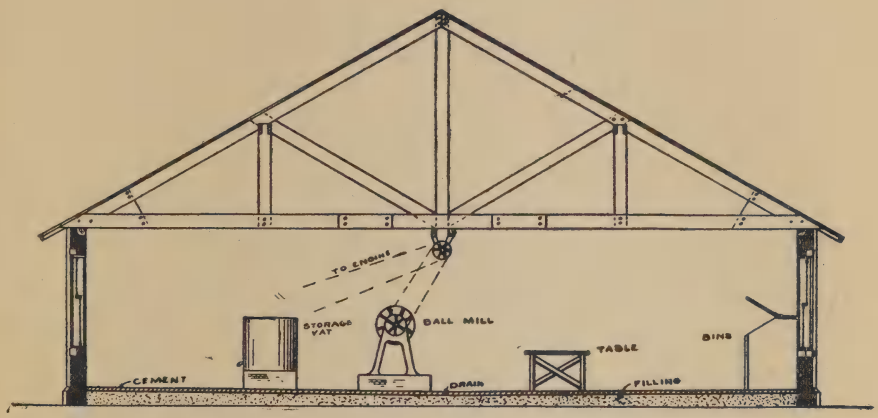
The structure is of brick, well lighted, and covered with a substantial slate roof. Cement floors are used, inclined to drains beneath each track so that the floors can be cleaned by flushing with a hose at any time. Cleanliness is all important in the enameling building. Dirt of any kind must not be allow to acccumulate.

For driving the slip apparatus (ball mill and blunger) a small gasoline engine would be preferable, on account of its cleanliness, and the fact that it is readily and economically worked periodically, for to get engobe and glaze for the capacity stated, the slip plant would run only on partial time.

The biscuit brick are brought in on cars and placed on the long tripple benches from whence, having been enameled, they are taken and placed on pallets, loaded on cars and run into the drying room. The drying room could more properly be termed the "storage room" for there is no need to dry the bricks. Usually a great many were carried to the kiln right from the dipping bench, being dried in the 12 hours wood firing which started the burning. The main purpose of the drying room was to take care of the bricks dipped in the periods when there was no kiln room for them.

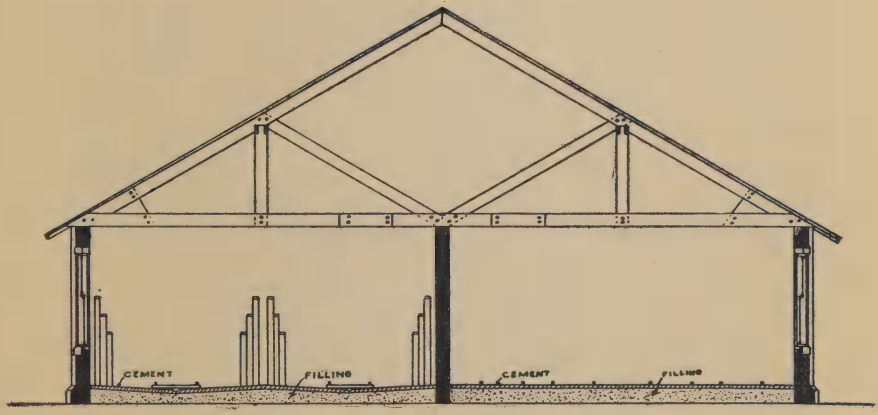
The kilns may be located near, preferably at the end opposite the slip-preparing room, so that the ware moves continuously forward. For kiln equipment, the writer favors square kilns of the Stewart type, in which the fire gases pass from the furnaces beneath the floor to bags on the opposite side. This type of kiln gives a very uniform distribution of heat.

The plant is designed for a very small capacity (4,000 brick daily) which may be increased, however, without much trouble. The given capacity is obtained by filling and emptying the benches twice daily, using one crew. To increase this to double or possibly triple, would merely mean filling and emptying the benches more often with several crews at work. The slip house is ample for three or four times the capacity stated, being designed to permit of enlargement.



SECTION ON B-B

SLIP ROOM



SECTION ON A-A

DIPPING AND DRYING ROOMS

PLANS FOR ENAMELED BRICK PLANT

DAILY CAPACITY 5000 STANDARD BRICK

SCALE, FT

The buildings shown in the above plates have not yet been constructed, but the process of enamelling is being carried on successfully on the original small scale as described above, at the works of the Columbus Brick & Terra Cotta Co., and the thanks of this society and the writer are due Mr. L. G. Kilbourne and Mr. Ellis Lovejoy, of this concern, for permission to publish this description of the work.

NOTE BY THE SECRETARY: This paper was read by title at the Boston meeting, and consequently received no discussion. Discussion is now specially invited, and if submitted in writing will appear in future volumes of these transactions.

THE GRINDING OF FLINT AND SPAR.*

BY

CHARLES F. BINNS, M. SC. ALFRED, N. Y.

(with 30 specimens and 5 micrograms.)

Scarcely a meeting of the Society has passed but some portion of this question has been introduced. It would seem as though there were a close agreement amongst us on two points, first, that our materials should be ground fine and, second, that this cannot be done.

The simple line of experiments discribed in this paper is an outcome of the thoughts expressed at previous meetings, and was undertaken with the view of throwing some light upon a vexed question.

Science can never be a partizan. It seeks truth and truth alone, and whether the truth be in accordance with our cherished beliefs or opposed to them, we want to find it.

The idea was to make up a series of bodies, similar in composition, by which the comparative action of coarse and fine materials should be illustrated.

SELECTION AND PREPARATION OF THE MATERIALS.

Kaolin.—The kaolin of the Hockessin Valley, Delaware, was chosen as a typical native kaolin.

The composition is:

Clay substance	90.42
Quartz	6.08
Feldspathic matter	3.50
	100.00

Ball Clay. — The brand selected is known as "Excelsior" and is sold by the Excelsior Ball Clay Company, Covington, Ky.

The composition is:

Clay substance	63.26
Quartz	35.00
Feldspathic matter	1.74
	100.00

*Read by title at Boston Meeting. Discussion specially invited.

Feldspar. — The ordinary spar of the Eureka Company, Trenton, N. J. was used.

The composition is:

Clay substance	4.28
Quartz	3.16
Feldspathic matter	92.56
	100.00

Flint.—The French Flint of the Eureka Company was assumed to be:

Quartz	100.00

It was washed successively through five lawns with the following results:

On 100 mesh, there was left nothing but a fragment or two of flint which had escaped grinding, and a small quantity of wood fiber from the linings of the cylinders, the flint having been ground dry in Alsing cylinders, lined with wooden blocks.

On 120 mesh was left	1.4%
On 140 " "	0.8%
On 150 " "	0.8%
On 160 " "	3.6%
Through 160 mesh	93.4%

Here let me say a word on the lawns used. Mr. Mayer added a note to the printed discussion of his paper published in the last Transactions, stating that there was a difference of standard as spoken of by different men. I want to say that he is right and I am wrong as reported.

The number of the lawn is the first two figures of the number of meshes to the linear inch, and the normal lawns in use in England are 14 and 16, No. 18 being only used for stain. This is as far as my experience goes.

I used 16 lawn as the finest in this experiment because, in my opinion, it will answer all the purpose. A lawn can never be an absolute test of fineness, its use is to separate unground particles, and not to gauge the size of the fine material.

A second sample of the same flint was taken and ground wet in a ball mill, until it seemed fine to the touch. This was also lawned through 16.

The residue of the unground flint left on each lawn

was now examined microscopically, and the grains measured. The sizes are expressed in the microscopist's unit "mu" (the Greek m) being of the value of one thousandth part of a millimeter. The size of the openings in the respective lawns is also given:

Grains left on	12	lawn measured	200 m			
" "	14	"	150 m	opening passed	140 m	
" "	15	"	120 m	"	"	123 m
" "	16	"	100 m	"	"	105 m
Passed through	16	(not ground)	80 m	"	"	87 m
Passed through	16	(ground)	20-40 m	"	"	87 m

These figures are instructive. It would be expected that a close correspondence would be found between the size of the opening in a lawn and the grain which passed through it, but I scarcely hoped that the figures would fit together so neatly. The fact that the grains are sometimes larger than the holes, is due to the shape of each. The holes are square and the diagonals are longer than the measured diameter, also the grains are quite irregular in form.

A sample of pan-ground flint was then examined for the sake of comparison and the following results secured:

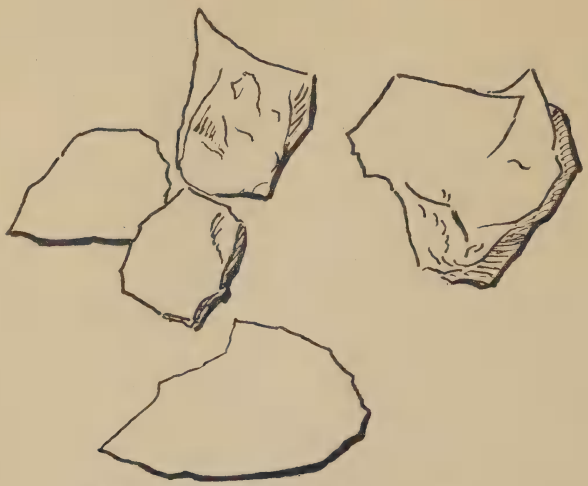
On 120 mesh was left	3.6%
On 140 "	4.5%
On 150 "	4.9%
On 160 "	2.8%
Through 160 mesh	84.2%

Thus as far as grinding is concerned, the sample of cylinder ground flint has the advantage, but of course this applies only to the actual samples handled.

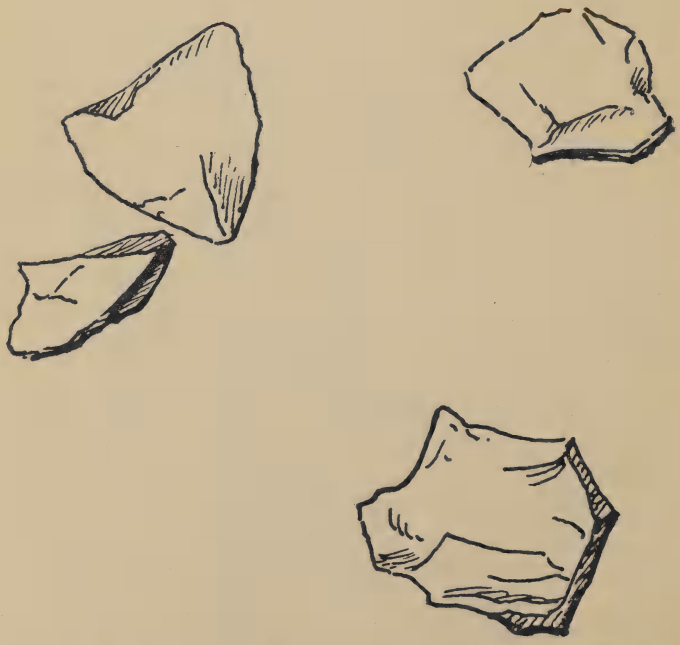
Microscopic examination of the pan-flint reveals the fact that the grains are similar in shape to those of the cylinder ground. It has been argued, especially by English potters, that the grains of cylinder flint are globular, while those of pan-flint are angular. In the samples examined by me this is not the case. The micrograms shown in Plates I and II, prove that there is no appreciable difference in the grains of pan-flint, cylinder-flint and cylinder-spar.

Micrograms of the unground and ground flint are also shown, in order to illustrate the relative size of grain. Both

PLATE I.



MICROGRAM, SHOWING SHAPE OF GRAIN OF CYLINDER-GROUND FLINT.



MICROGRAM, SHOWING SHAPE OF GRAINS OF PAN-GROUND FLINT, OF SAME MAGNIFICATION.

PLATE II.

MICROGRAM SHOWING SHAPE OF GRAIN OF CYLINDER-GROUND FELDSPAR, SAME MAGNIFICATION AS FLINT.

have passed through 16 lawn but the second has been ground as discribed. (See Plate III.)

Both flints were dried after lawning and labelled "Sifted flint" and "Ground flint" respectively. Pan-flint was not used.

Feldspar: The normal body-spar of the Eureka Co. was treated in a similar manner.

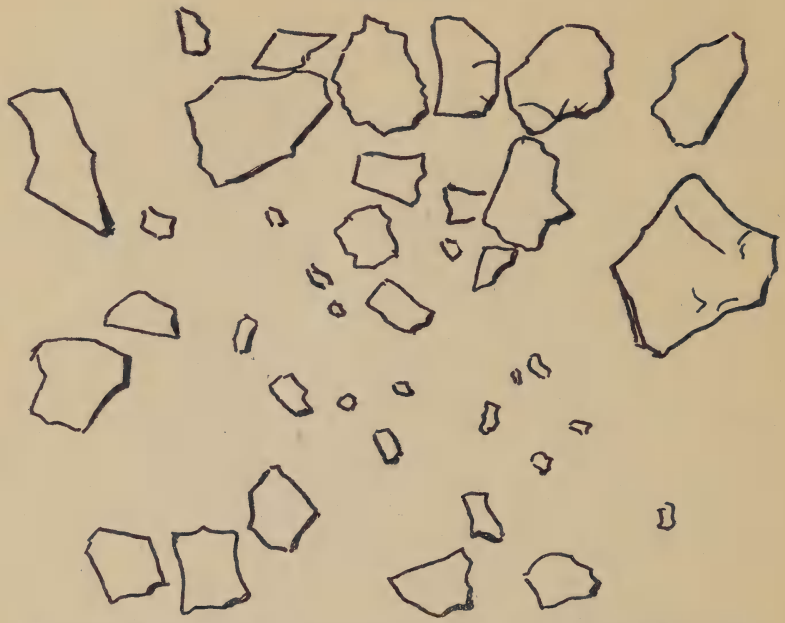
On 100 mesh	was left	3.6%
On 120	"	1.7%
On 140	"	2.7%
On 150	"	1.2%
On 160	"	2.2%
Through 160 mesh		88.6 %

A second sample was then ground fine. This, under the microscope, was found to be almost identical in size of grain with the ground flint.

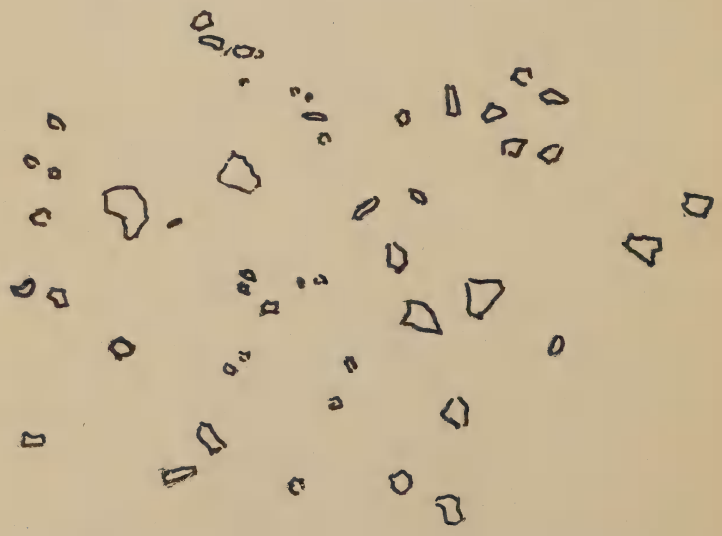
MIXING THE BODIES.

It was decided to maintain the clays at a constant ratio because the experiment was only concerned with flint and spar.

PLATE III.



MICROGRAM, SHOWING DRY-GROUND CYLINDER FLINT, WHICH HAD BEEN PUT THROUGH 160 MESH LAWN. MAGNIFIED 250 DIAMETERS.



MICROGRAM, SHOWING SAME FLINT AFTER GRINDING IN WET BALL MILL, AND PUTTING THROUGH 160 MESH LAWN. MAGNIFIED 250 DIAMETERS.

Four series were projected which should contain respectively:

I Sifted flint and normal spar
II Ground flint and normal spar
III Sifted flint and ground spar
IV Ground flint and ground spar

and each series was to consist of three members containing:

No. 1	Flint	40	Spar	10
No. 2	"	30	"	20
No. 3	"	20	"	30

in accordance with the table below:

SERIES I.

No.	Kaolin.	Ball Clay.	Sifted Flint.	Normal Spar.
1	20	30	40	10
2	20	30	30	20
3	20	30	20	30

SERIES II.

No.	Kaolin.	Ball Clay.	Ground Flint.	Normal Spar.
1	20	30	40	10
2	20	30	30	20
3	20	30	20	30

SERIES III.

No.	Kaolin.	Ball Clay.	Sifted Flint.	Ground Spar.
1	20	30	40	10
2	20	30	30	20
3	20	30	20	30

SERIES IV.

No.	Kaolin.	Ball Clay.	Ground Flint.	Ground Spar.
1	20	30	40	10
2	20	30	30	20
3	20	30	20	30

The rational composition of each series is identical, and and works out as follows:

	Clay Substance.	Quartz.	Feldspathic Matter.	Total.
No. 1—	37.3	52.1	10.6	100
No. 2—	37.8	42.4	19.8	100
No. 3—	38.3	32.4	29.3	100

The whole of the twelve bodies were weighed up, blunged, and lawned through No. 10 to break up the clay and secure a perfect mix. A portion of each slip was used to cast a small vase, and the remainder was made into clay and pressed into plaster molds to form small slabs, thus showing the structure of both cast and pressed ware.

In order to throw light upon the mutual reactions of clay, flint and spar, two more series were prepared:

SERIES V.

No.	Kaolin.	Ball Clay.	Sifted Flint.	Ground Flint.	Normal Spar.
1	..	..	50	..	50
2	..	..	..	50	50
3	20	30	..	..	50

SERIES VI.

No.	Kaolin.	Ball Clay.	Sifted Flint.	Ground Flint.	Ground Spar.
1	..	..	50	..	50
2	..	..	..	50	50
3	20	30	..	..	50

In these six trials, the relative action of spar in each condition upon flint in each condition and upon the normal clay blend is illustrated.

The mixtures of spar and flint were worked with mucilage to provide an artificial plasticity, those of spar and clay were treated as before described. The whole were made up into small plaques, and, with the members of the first four series, placed in the same sagger with the cones exhibited and fired to cone 9. The firing was maintained (natural gas being the fuel) during 14 hours in an oxidizing atmosphere. The cooling took 26 hours.

The whole of the bodies were vitrified and the other features presented are tabulated below:

SERIES I.

No.	Texture.	Color.	Ink Test.
1	Granular	Cream	Slowly absorbed
2	Granular	Stony	Slightly retained
3	Granular	Stony	Slightly retained

SERIES II.

1	Dense	Cream	Slightly absorbed
2	Porcellanous	Stony	No absorption
3	Porcellanous	Stony	No absorption

SERIES III.

1	Granular	Cream	Slightly absorbed
2	Granular	Stony	Slightly retained
3	Granular	Stony	Slightly retained

SERIES IV.

1	Dense	Cream	Slight absorption
2	Porcellanous	Stony	No absorption
3	Porcellanous	Stony	No absorption

The "ink test" consists in drawing a pen full of ink across a broken surface. Some times the ink is drawn into the pores of the body, some times it spreads through the irregularities of the granular surface, and some times it remains where placed and can be washed off without a stain. The test is not exactly scientific, but it is one with which all potters are familiar and is, moreover, used as a decisive test of quality by some buyers. The comparison of the trials for determining the effect of grinding will lie between Series I, where both materials are crude; Series II, where the flint alone is ground; and Series III, where the spar alone is ground.

In Series I, numbers 2 and 3, a granular structure is observed, with complete vitrification, but the coarse grains allow the ink to spread. There are also numerous brilliant specks due to fragments of spar. These specks disappear in Series III, but the structure appears otherwise unchanged.

In Series II, however, an important alteration is noticeable. Here the flint has been ground but not the spar. The granular fracture is lost, and in its place there is a fine porcelain texture upon which the ink has no effect whatever. This is maintained in Series IV, the only difference being that the bright specks before alluded to disappear.

The evidence so far is that the grinding of flint has a very marked effect, but that the grinding of spar has less. This seems to be the case, whether flint or spar is in excess. Body No. II-2 with 30 per cent. ground flint and 20 per cent. normal spar, is as vitreous as No. III-3 which has 20 per cent. sifted flint and 30 per cent. ground spar. The argument from this is that if the flint be fine, the influence of the spar will be increased, whether it be fine itself or not.

Turning now to the later series, V and VI, some interesting evidence is found. The relative action of ground flint and ground spar is in accordance with that stated above, but the action of the spar on clay is most instructive. The value of ground spar is shown better here. It becomes much more powerful by grinding. On comparing VI-3 with V-3 we notice the higher vitrification of the former.

The blends of spar and clay alone have the appearance of a frit or slag. They seem to be not translucent, but transparent, and to this fact is due their dark color. The mixtures of spar and flint seem not less vitreous or translucent, but they lack the glass-like transparency which the clay mixtures possess. From this argument may be deduced that clay substance, perhaps because already in combination, dissolves in the fused spar, while the flint, being free silica, remains in suspension.

A new light is thus cast on the problem of color and translucency. Spar appears to render the clay mass transparent and dark, because the rays of light penetrate and are not reflected. The effect is similar to that of a depth of water; the color becomes dark by the absorption of light, even tho the water itself be colorless. But now, if a sudden agitation of the water takes place, and numerous air bubbles be formed, the whole becomes a pearly white, translucent still, but the darkness is lost. So when in the fused mass of spar

there are present a large number of flint fragments, the reflection from these imparts whiteness, and through the spaces between them the light rays can pass. Add to this the fact that most of the flint grains are in themselves translucent, and there is an explanation of the combined whiteness and translucency in the presence of flint, which does not occur in its absence. Obviously then the fine grained flint will have a stronger influence, for there are just so many more points for the reflection of the light rays.

The grinding of spar has the effect of increasing its power at a given temperature. The fragments of spar, rendered fluid by heat may be likened to a number of pools of liquid, charged with the duty of joining with each other over an intervening space of solid ground. If these pools be separated into smaller portions, their size being one-fourth and their number four times as great, it is obvious that the solid ground will be covered so much more thickly and the distance between the pools correspondingly reduced. The effort to join each other will not be so great, and energy will be economised.

Now, since this energy is in the form of heat, and fuel costs money, it is certain that a reduction in the size and an increase in the number of spar particles means a saving. In addition to this, the reduction in the size of the liquid points means a more uniform mass. There is less danger of blistering from unequal distribution of flux, and there is an economy of material.

It may be argued by some that finer grinding of flint and spar means more shrinkage, and a consequent expense, in some cases, for new molds. But it will be found that, with the materials properly ground, it is possible to increase the flint and lower the spar, thus helping to maintain the size and affording a whiter body.

The evidence of this experiment is strongly in favor of fine grinding, and the time will surely come, and that quickly, when the progressive potter will formulate a demand in this direction which will admit of no denial.

Discussion by Lawrence E. Barringer,*
Schenectady, N. Y.

On the subject of fine grinding of flint and feldspar I should like to have Mr. Binns asked whether he has noted any change in the chemical behavior of feldspar after long, continued grinding. Of course, in the case of flint, fine grinding is not accompanied with any chemical change, but geologists in studying rock decomposition have found that natural silicates may be decomposed by grinding with cold water. Daubree found on rotating angular fragments of feldspar in an iron barrel with water at a velocity of one metre per second, that they gave .003 of their weight of clay *per kilometer*. Further, he took *three* kilograms of orthoclase and rolled in an iron barrel for 192 hours (460 kilometers) and found that it gave 2.7 kilos of clay and that 12.6 grams of K_2O were set free as silicate. Distilled water was used. The experiment proved that feldspar may be decomposed by water alone and even by cold water, forming kaolin and alkaline silicate. M. Heim, in investigating the settling of pottery glazes, also found that long continued grinding of frits resulted in the separation of free alkali, which caused the glaze to set hard in the bottom of the mill. I am interested, therefore, in knowing whether it is possible to seriously affect feldspar from a potter's standpoint by wet grinding it for long periods.

*Communication sent in to the Secretary.

NOTE ON FINE GRINDING OF GLAZES.

BY

OWEN CARTER, POOLE, ENGLAND.

I notice in a paper on page 64 of Vol. I, of the Transactions, the writer says:

"All these glazes could not be used in commercial work as they carry too much frit. They settle too quickly, and are very irregular in dipping."

The experience my firm have had on this subject may be of interest, if not of use to some members.

The English potters have been for some time fearing the passing of some kind of legislation prohibiting the use of glazes of high solubility as regards lead.

The difficulty was that if one made a frit to meet the proposed government requirements, an 07 or 08 fire was necessary (our usual heat). It was, therefore, very evident that no raw flotative ingredients could be added, raw lead being forbidden, and soft alkaline frits being impractical for various reasons.

The only thing to be done was to use the pure frit, and then came the difficulty of settling; etc. If the frit was ground wet in the usual way, fine enough to keep in suspension in water for dipping, the glaze on the surface of the tiles, when the water had dried out, would become covered with fine cracks, and upon firing, the glaze would peel up and collect into beads or patches on the surface leaving bare places. Thin dipping, such as is practiced with earthenware, would prevent this, but colored glazes on tiles must be dipped thickly.

The solution of the problem was found in grinding the frit dry in Alsing cylinders. I only recollect one case of peeling up with a dry ground glaze. It seems almost impossible to dry-grind it too finely. I do not say that too fine grinding is in every case the reason of glazes peeling and

gathering into patches and beads; but I think that this is usually the cause. Fortunately it can generally be noticed before the tiles are fired, if one is on the look-out for it, as after dipping and standing a little time and drying, the surface of the tile will be noticed covered with these very fine cracks, especially where the glaze is thick.

The firm I am connected with being anxious to do away with the use of raw lead in their glazes, use a frit of low solubility wherever possible. Probably two thirds of the total glaze used at their works is just the pure frit, without the addition of any raw material. It is, however, impossible to use it for all the colors.

THE EFFECT OF FINE GRINDING IN THE MANUFACTURE OF BEDFORD SHALE BY THE DRY AND PLASTIC PROCESSES.

BY

W. G. WORCESTER, PARKERSBURG, W. VA.

In the economic value of the Ohio clay deposits, the red Bedford Shale plays an important role. This is a clay of peculiar and striking characteristics, valuable to the manufacturer for several reasons: First of all, it produces on burning one of the most magnificent red colors known, probably the finest red color of any clay in the United States. In addition to this, it possesses the property of vitrifying at a slow and safe rate, since its point of vitrification and its melting points are separated by a wide interval. Further, it retains its fine red color even when vitrified, being the only clay known to the writer which does so. This red color owes its source to the presence of finely divided ferric oxide, already indicated by the chocolate color of the shale. In texture, the shale is extremely fine grained, and is readily made up to a plastic body. In addition, the bed appears to be remarkable in uniformity of composition and character.

These properties are, however, counter-balanced to some extent by the comparatively large shrinkage, and the fact that its fine and dense body renders it hard to burn, owing to the internal gases at the vitrifying point being unable to escape, thus causing bloated or blistered ware unless burnt slowly.

It is now the purpose of this paper to show how the characteristics of this clay, its magnificent red color, and its property of retaining this color at vitrification, may be retained and its disadvantages eliminated, making this elimination complete and increasing the safe burning of the clay.

It has not been known until quite recently, outside of the circles of geologists, that red Bedford Shale is found at more than one point in the state, that being at and near South

Park. However, it is now known to be found at various points from the lake shore to within a short distance of the Ohio River. As before said, it was found at South Park, and near Cleveland; at Elyria, there are beds from twenty to thirty feet thick. The Vermillion River received its name from the fact that its banks near Brownhelm are composed of beds of the red Bedford Shale over forty feet thick, and the waters of the river washing this red deposit are colored red, hence the name Vermillion. Passing south in the state it is again reported at Leesville, Crawford County, next, at Galena and Sunbury, Delaware County. And from the latter place south, it has been traced uninterruptedly for a distance of fifteen miles by the writer. A typical section on this line is about as follows:

Berea Grit	0 to 30 feet.
Chocolate Shale (Bedford)	10 to 40 feet.
Green or Olive Shale (Bedford)	0 to 20 feet.
Black Shale (Huron)	(Unknown depth.)

At Taylors's Station there is a fine deposit that is to be worked this year for the first time. It was from this deposit that the samples for these tests were taken. Passing on south of Taylor's Station it again crops out near Marcy, Fairfield County. Then further south large deposits of it are found at Waverly and Piketon; though as it passes south, the red chocolate color gradually disappears and is replaced by a blue or gray colored material. So it can plainly be seen that this deposit is more widely distributed than has heretofore been known by clay workers. It has only been worked at one point, Independence, Ohio, being there made into the famous Akron Red pressed brick, a color which it was thought could not be reproduced elsewhere.

The practical question now arising is that of the reduction of shrinkage by some non-plastic material. The following "leaning" or non-plastic substances are available under ordinary conditions; first, the use of grog from the same clay, which will reduce the drying but not the burning shrinkage; second, the use of fire-clay grog, which will reduce both the drying and burning shrinkage, but will practically spoil the color; third, the use of sand, which will do away with shrinkage, but is very apt to affect the color materi-

ally, and is liable to introduce undesirable impurities owing to its varying composition. Hence, none of these three are perfectly satisfactory.

I have discovered the fact that the Berea Grit, a fine-grained sandstone of uniform composition which invariably accompanies the Bedford Shale, assumes on burning a reddish color. This suggested the use of this stone as a non-plastic material most suitable for reducing the shrinkage of the shale. No economic objection can be offered to this argument, and there only remained to prove by actual experiment its influence upon the color, shrinkage and texture of the burned shale.

The plan of the experiments carried out is as follows:

First. It was necessary to determine the shrinkage of the shale by itself, and at the same time to inquire into the effect of grinding the shale coarser or finer. I also found it necessary to determine the properties of the shale shown in working by the plastic and dry-press processes. I therefore prepared the all-clay series as follows:

No. 1—All clay, over 100 mesh.
No. 2—80 per cent. No. 1, 20 per cent. clay, 8 to 20 mesh.
No. 3—80 per cent. No. 1, 20 per cent. clay, 20 to 40 mesh.
No. 4—80 per cent. No. 1, 20 per cent. clay, 40 to 60 mesh.
No. 5—60 per cent. No. 1, 40 per cent. clay, 8 to 20 mesh.
No. 6—60 per cent. No. 1, 40 per cent. clay, 20 to 40 mesh.
No. 7—60 per cent. No. 1, 40 per cent. clay, 40 to 60 mesh.
No. 8—40 per cent. No. 1, 60 per cent. clay, 8 to 20 mesh.
No. 9—40 per cent. No. 1, 60 per cent. clay, 20 to 40 mesh.
No. 10—40 per cent. No. 1, 60 per cent. clay, 40 to 60 mesh.

Second. It was also necessary to prepare shale mixtures in which the crushed Berea grit is incorporated, analagous to the mixtures of the all clay series; for this purpose, the sandstone was crushed and screened similarly to the shale, and the following mixtures prepared:

No. 1—All clay, over 100 mesh.
No. 02—80 per cent. No. 1, 20 per cent. stone, 8 to 20 mesh.
No. 03—80 per cent. No. 1, 20 per cent. stone, 20 to 40 mesh.
No. 04—80 per cent. No. 1, 20 per cent. stone, 40 to 60 mesh.
No. 05—60 per cent. No. 1, 40 per cent. stone, 8 to 20 mesh.
No. 06—60 per cent. No. 1, 40 per cent. stone, 20 to 40 mesh.
No. 07—60 per cent. No. 1, 40 per cent. stone, 40 to 60 mesh.
No. 08—40 per cent. No. 1, 60 per cent. stone, 8 to 20 mesh.
No. 09—40 per cent. No. 1, 60 per cent. stone, 20 to 40 mesh.
No. 010—40 per cent. No. 1, 60 per cent. stone, 40 to 60 mesh.
No. 011—70 per cent. clay, 30 per cent. stone, ground in ball mill three hours.

The shale was put through a small jaw crusher which reduced it until it passed through an eight mesh screen; it was next thrown onto a twenty mesh screen, and carefully sifted; all that remained on the twenty mesh was saved; the part that has passed the twenty mesh was put onto a forty mesh and sifted again; what remained on the forty mesh was put aside. The portion which was finer than the forty was sifted on a sixty mesh, and the part that did not pass through it was saved. The balance of the material was then sifted on the hundred mesh screen, and that which passed through it was taken as the starting point for all of the tests.

The various mixtures were then weighed out and mixed by passing them through sieves and repeated stirring. For the dry press tests, the different batches were placed in a clean enameled pan, one at a time, and mixed with water until each seemed to have the proper amount for dry pressing. As soon as each was supplied with its requisite amount of moisture, it was placed in a fruit can, screwing the top down tight and allowing it to stand for forty-eight hours, so as to distribute the moisture evenly throughout the mass.

For the plastic tests, the mixtures were taken one at a time in a clean basin, and water added until they could be worked nicely by the hands; it was then worked well to free it from air as far as possible, and was then molded at once into small brickettes, using brass molds such as are used for making cement brickettes for tensile strength tests. As soon as removed from the mold, they were each in turn weighed very accurately, and shrinkage marks made upon them by means of a very thin spatula. The brickettes were then placed upon smooth boards, and allowed to dry slowly until leather hard; they were then put upon racks above a hot plate, and the heat was slowly increased until they were to all appearances dry. Taking them from the racks they were placed in small drying ovens, and kept at 120 degrees C for three hours; removing them from the oven while hot, they were placed in dessicators until cool, and then weighed and also measured, to note the drying shrinkages and percentage of water used for mixing.

The work of making the dry press tiles was done as follows: The mixtures which had been placed in the fruit cans were taken to a testing machine used for making crushing and cross-breaking tests in the mechanical department the of Ohio State University. A die two inches by two inches was used, and the machine set to give 12,000 pounds pressure per square inch; as it was desired to have every tile receive the same pressure, and knowing that anything like accurate results could not be obtained by trying to guess at the amount of pressure applied to each. As soon as removed from the die, they were numbered, and a mark made with a knife from side to side from which the shrinkage was measured. These tiles were also weighed at once, and were dried in the same manner as the plastic, except that they were placed over the hot plate immediately. After allowing them to cool in the dessicator, they were weighed again and each tile was measured for shrinkage, but the shrinkage, if any, had been so slight that it was impossible to measure it.

PER CENT. OF WATER.

All-Clay Series.			Stone Series.		
No.	Dry Press.	Plastic.	No.	Dry Press.	Plastic.
1	5.2%	20%	1	5.2%	20%
2	4.5	11	02	6.2	24
3	6.3	20	03	6.6	19
4	4.8	20	04	9.3	15
5	6.7	17	05	5.7	16
6	9.3	19	06	1.4	18
7	9.3	19	07	7.8	18
8	7.3	18	08	3.9	13
9	8.4	12	09	6.6	16
10	7.5	19	010	7.8	15
			011	6.6	23

BURNING.

In the carrying out of this part of the investigation, a small rectangular down-draft kiln at the ceramic department of the Ohio State University was used, The tile and brickettes were packed in a sagger rather closely, though using clean white sand between each. The sagger was then placed as near the center of the kiln both vertically and horizontally as possible; bricks were then set around the sides

and over the top of the sagger in order to hold the heat as even as possible. From a previous trial-burn, it was known that cone 06 would bring this clay to a good sound body, though not vitrified, so for this burn cones 07, 06 and 05 were placed immediately in front of the sagger and in the sagger. The firing was proceeded with in the usual way using soft coal and gas coke for the fuel. At the end of twenty-eight hours, cone 07 was nearly down and 06 started, so the fire was allowed to burn clear and the damper lowered; the kiln was then allowed to cool twenty-four hours, after which time the ware could be handled.

The various trials were then measured again, and each one weighed; they were immersed in distilled water for a period of forty-eight hours; they were then taken out one at a time, the surface water wiped off with a clean towel, and weighed at once. This gives the weight of water absorbed as a measure of porosity.

RESULTS OF THE BURN.

All Clay Series, Dry Press.

In selecting the most suitable mixture, the points taken into consideration were: first, color; second, shrinkage; third, porosity; fourth, indications of proper burning. In the accompanying table all the data obtained are collected; it will be seen that the densest mixtures show black cores, indicating difficulty of burning which must rule out these mixtures. With coarser grains, the difficulties of burning disappear and at the same time neither the burning shrinkage nor porosity are increased. The mixtures selected are first number 3, whose composition is 80 per cent. clay over 100 mesh, 20 per cent. clay 20 to 40 mesh and which when made up with 6.33 per cent. water will give 4.43 per cent. burning shrinkage and 3.48 per cent. porosity. The second best is number 10 whose composition is 40 per cent. clay over 100 mesh, and 60 per cent. clay 40 to 60 mesh, and when made up with 6.63 per cent. water will give 3.13 per cent. burning shrinkage and 7.74 per cent. porosity.

No.	Appearance.	Remarks.
1	Black Core nearly throughout.	Rejected on acc't of Black Core.
2	Black Core 4-5 cross section.	Rejected on acc't of Black Core.
3	No Black Core.	Accepted. (Best.)
4	Black Core ½ cross section.	Rejected. Black Core.
5	Black Core ¾ cross section.	Rejected. Black Core.
6	No Black Core.	Fifth best.
7	No Black Core.	Fourth best.
8	Signs of Black Core.	Rejected. Too coarse.
9	Signs of Black Core.	Third best.
10	Color exceptionally good.	Second best.

All Clay Series, Plastic.

The selections of the most suitable mixtures in this series was rendered somewhat difficult by the fact that they were under-burned, so that the proper color selection could not be made. Black cores were only shown by two mixtures, Nos. 1 and 2. All that could be done in this series was to judge the color from the corresponding colors of the dry-press series which were burned harder, and to select the mixture showing the lowest shrinkage and porosity. The most favorable mixtures are Nos. 7 and 8. Number 7, whose composition is 60 per cent. clay over 100 mesh and 40 per cent. clay 40 to 60 mesh with 19 per cent. water, gives 9.37 per cent. total shrinkage and 6.8 per cent. porosity. The second best, number 8, whose composition is 40 per cent. clay over 100 mesh, and 60 per cent. clay 8 to 20 mesh, when mixed with 18 per cent. water gives 8.6 per cent. total shrinkage and 7.66 per cent. porosity. The data are shown in the following table.

No.	Appearance.	Remarks.	Drying Shrinkage.	Burning Shrinkage.	Total Shrinkage.	Porosity.
1	Good color 1-3black	Rejected	6.80	5.70	12.50	8.11
2	Good color ½ black	Rejected	6.25	4.69	10.94	6.10
3	Soft burned		6.25	3.91	10.16	7.27
4	Soft burned		7.81	4.70	12.50	5.79
5	Soft burned	2nd best	5.86	3.13	8.99	7.90
6	Soft burned	3rd best	6.25	3.91	10.16	7.24
7	Soft burned	1st best	5.47	3.90	9.37	6.80
8	Soft burned		5.47	3.12	8.59	7.66
9	Soft burned		7.42	2.74	10.16	7.23
10	Soft burned		6.25	4.69	10.94	5.63

Stone Series, Dry Press.

Numbers 02, 05, 06, 08 and 09 were rejected on account of either pale color, or being rough on the surface due to sand grains. The most favorable mixtures are 03 and 011, the latter however, having the defect of showing some lamination. The cause, however, is not fully determined, as it may be due to the high pressure, or due to too much or too little water, or too great fineness of grain. Number 03 when made up with 6.6 per cent. water, showed 2.4 per cent. total shrinkage with 7.15 per cent. porosity. Number 011 when made up with 6.63 per cent. water, showed 3.13 per cent. total shrinkage and 7.74 per cent. porosity. The data are not published in full, but the four best mixtures are selected for the following table.

No.	Remarks.	Drying Shrinkage.	Burning Shrinkage.	Total Shrinkage.	Porosity.
03		None	2.42		7.15
04	Selected, as the best	None	2.28		17.71
07	of the Dry-press Series.	None	1.72		10.95
011		None	3.13		7.74

Stone Series, Plastic.

None of the mixtures in these series showed any black cores whatever; they suffered the defect of not having been burned enough. Number 011, having for its composition 70 per cent. clay, 30 per cent. stone, and having been ground in a ball mill for three hours, showed defect of being laminated quite strikingly, which suggests that it is too fine. Numbers 04 and 07 were the most suitable mixtures, 04 with 15 per cent. water shows 8.6 per cent. total shrinkage and 8.8 per cent. porosity. Number 07 with 18 per cent. water showed 7.42 per cent total shrinkage and 10.55 per cent. porosity. These porosities can only be considered as relative values, since when burned to the proper temperature they would show a much smaller percentage. But it is evident that any gain in decreased shrinkage is to some extent balanced by the increased porosity. The same four mix-

tures are here also the best, and are shown in the table below.

No.	Remarks.	Drying Shrinkage.	Burning Shrinkage.	Total Shrinkage.	Porosity.
03		2.34	5.47	7.81	11.26
04	Selected, as the best	4.69	3.90	8.59	8.84
07	of the Plastic Series.	5.47	1.95	7.42	10.55
011		6.25	3.91	10.16	10.77

GENERAL CONCLUSIONS.

A remarkable fact noticed in this test was that both of the dry press series, though burned with the plastic trials showed a better color and greater hardness. From the results before us, the conclusion to be reached would be that where dry pressing is practiced, no addition of sand is necessary. It might pay to use a small proportion of 60 to 100 mesh stone, say about 10 per cent, as this will facilitate the proper burning of the ware by opening up its pore system to a small degree, and thus tend to prevent bloating. However, greater care should be taken to properly size the grains of clay than is now being done in most brick works. For the red Bedford Shale, the most suitable combination of sizes is shown by Number 3, followed by Number 10.

On the other hand, where it is necessary to work the red Bedford Shale by the plastic process, as for roofing tile, paving brick, stiff-mud face brick, machine-made terra cotta, etc., ground stone mixture should be used. The most suitable mixtures are the compositions of numbers 04 and 07; in addition to decreased shrinkage, another great advantage is the increased safety of burning, which will shorten the time and decrease the loss of ware due to black cores and will soften it considerably. These advantages, therefore, greatly overbalance the somewhat greater porosity.

One great advantage of the plastic stone series is that over-burning cannot occur. Even in careless burning, bloating is made almost impossible. This last statement was verified by myself, in an experiment in which I made cones of

both the *all clay* and *stone series*, burning them to a temperature of 1,300°C, in a reducing fire. The all clay cones were badly bloated and blistered and had melted down, while on the other hand, the sand series though vitrified, had either commenced to fuse smoothly, without bloating, or were still in an unfused condition.

The cone tests showed very consistently a very peculiar fact which was unexpected to me; this was that the mixtures highest in stone, 60 per cent, were the most fusible ones, which is contrary to the laws of fusibility applied to ferruginous clays, but in accordance with the laws referring to the refractory clays. One explanation which suggests itself, is that iron of the clay may have been drawn into reaction with the silica, forming a fusible iron silicate which started the fluxing action, and caused the cones to fuse earliest.

ON THE PRODUCTION OF AN EASILY FUSIBLE GLASS WITHOUT THE USE OF LEAD OR BORACIC-ACID.

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I. Purpose of the Investigation.

In the last two meetings of this Society, papers have been read and discussions have been had on certain defects of the Seger cone as a means of control for the burning of clay wares. The criticisms raised have been directed almost entirely to that part of the cone series devised by Dr. E. Cremer of Berlin, which was grafted onto the original series developed by Dr. Seger, some time after the latter had been brought to public attention, and also to the lower three members of Seger's series, in which Fe_2O_3 is used as a flux. These criticisms have not been directed to the Seger cones free from iron, nor to the recent series devised by Dr. Hecht for the measurement of temperatures below 950°C.

The various charges which have been made and substantiated against these ferrugineous cone mixtures are as follows:

1st. It has been shown by Gorton[1] that the presence of ferric oxide as a flux constitutes a source of irregularity in their heat reactions, from the fact that Fe_2O_3 is easily reducible to 2 FeO, by CO or CH_4 or H in the kiln gases, and that FeO is known to cause fusion in a silicate mixture at temperatures much lower than Fe_2O_3 will do. Wheeler gives the difference as amounting to 200 deg.C, and while the writer is unable to find other support for this statement, his own experience confirms it, at least so far as agreeing that the difference is a considerable one. A silicate which is designed to fuse uniformly at one temperature, should at least avoid the use of fluxes which can, by mere variations

1 Trans. American Ceramic Society, Vol. II, pages 60-64.

in the firing, develop considerable difference in fusing point.

2nd. The use of a boro-silicate frit as the basis of the Cremer series has been condemned. It has been pointed out by Hottinger[1] that boracic acid is a very volatile constituent, which not only escapes by volatilization, but is easily set free from its compounds by SO_3 in the kiln gases, and thus expelled much more rapidly than would be the case, if it were heated in pure air alone. This fact has been used to explain the "drying out" of the tips of the cones; the formation of a hard shell, and a molten interior; the failure to bend at the proper time, and other defects of the Cremer cones.

3rd. The formation of $CaSO_4$ from the $CaCO_3$ used in the cone series, or from the CaO formed by the breaking down of the latter, has also been pointed out as a fruitful cause of trouble, especially in the low temperature cones. In firing kilns at low temperatures, the kiln gases are generally maintained in oxydising condition, and thus no opportunity occurs to expel the SO_3 by reduction to SO_2, which generally does take place, intentionally or otherwise, when the kiln is to reach a temperature above cone 1. The CaO which goes into combination with SO_3 is supposed to be withdrawn from duty as an active flux, until the acid is finally expelled. Meanwhile, the fusion of the cone is supposed to be delayed for the lack of the requisite quantity of effective flux.

All three of these charges are based upon numerous authenticated cases, in which it has seemed clear that the reason assigned has been undoubtedly to blame for the trouble. For instance, Gorton showed that by omitting iron from his cones, that he greatly improved their behavior. Hottinger showed that cones and glazes of the same composition, fired in the open kiln were defective as described, while fired in saggers washed with lime to intercept the SO_3, the same cones and glazes behaved perfectly. Lastly, the writer has found that cones which failed to fuse at the proper temperature, and which swelled badly on fusion, con-

1 Trans. American Ceramic Society, Vol. II, page 65—Vol. III, page 180.

tained 2.5 per cent. of sulphur which was not in the cone when placed in the kiln, and which had undoubtedly been absorbed from the gases during firing, and which undoubtedly prevented normal fusion.

The writer has undertaken the following investigation with a view to ultimately producing a series of cones which will occupy the temperature range now covered by the Cremer series, but which will avoid wholly or in part the above defects. The principal points in which it seems that such an improved series should differ from that of Dr. Cremer, are:

1st. The omission of iron oxide as a flux, and its substitution by some other oxide not subject to easy reduction.

2nd. The replacement of the boro-silicate frit by one less volatile, and less easily attacked by acid kiln gases.

3rd. The cessation of the use of lime and other strong bases in the form of carbonates or oxides, which invite the formation of sulphates during the early portion of the burn.

II. General Method of Attack.

It is obvious at the outset, that these limitations threaten to make the task a somewhat difficult one. There remains commercially available for use only the following oxides, capable of making colorless or white silicates:

$$\left.\begin{matrix} K_2O \\ Na_2O \\ CaO \\ MgO \\ BaO \\ ZnO \end{matrix}\right\} Al_2O_3, SiO_2$$

with the possible addition of P_2O_5, as an available acid. These substances may be compounded into a frit or may be used raw in any form which will gain the end in view.

But little experience is required in the compounding of raw stoneware glazes, to know that with this preceding list of availables, no raw or unfritted mixture fusing at the melting point of cone 010, or 950 deg. C can be made. In fact, excluding BaO, no glaze can be made from the others which fuses below cone 1, without resorting to other sources of alkali than feldspar, which is impractical in cone manufacture. The use of BaO has not been extensively tried by the writer,

but the results where tried were such as to indicate that it would not greatly reduce the point of initial combination, though quite fusible after combination had been once perfected. Hence, fritting must be accepted at the outset as absolutely essential to any successful effort.

Dr. Hecht has pointed out[1] that the proper compounding of a low temperature cone mixture requires a frit or a fusible glass base, and a certain amount of raw or unfritted materials. The frit cannot properly exceed a certain proportion of the total mixture, because glasses soften and pass from rigid solids into liquids so rapidly that cones made largely from them would be too sensitive, and would not undergo a gradual vitrification and gentle fusion. The raw ingredients play an important part in holding up the body mass, and requiring an appreciable time to complete their vitrification and fusion, even after the glass has fused completely.

III. Attempt to Use Common Glass.

The first experiment made was to use common lime-soda glass as the frit, as it can be had cheaply and abundantly.

Its average composition may be taken as

$$\left.\begin{matrix}0.5\ Na_2O\\0.5\ CaO\end{matrix}\right\}2.50\ SiO_2$$

Accordingly, a lot of scrap glass was procured, and ground in a wet ball-mill, till it readily passed through a 150 mesh screen. This was dried and weighed as a fine powder. The formula of the first test mixture was roughly:

$$1\text{-A} — \left.\begin{matrix}0.3\ Na_2O\\0.7\ CaO\end{matrix}\right\}0.3\ Al_2O_3,\ 2.10\ SiO_2$$

The alkali, 0.3 eqv. of the lime, and 1.50 eqv. of the silica were derived from the glass, while 0.4 eqv. lime was supplied as bone ash, under the hope that the latter might be used as a source of lime, which would not open up the troubles incident to the use of $CaCO_3$ in its commercial forms. The alumina was supplied as kaolin, so that the batch weights of the mixture were:

1-A —	Powdered window glass	41.8
	Calcined bone	13.7
	Kaolin	25.8
		81.3

1 Thon Industrie Zeitung, Vol.—, page 189.

These ingredients were ground intimately together, dried, mixed with dextrine paste, and molded into test cones, which were then tested against the regular cones from 010 to 1.

The glass-bone-kaolin mixture fused a little later than cone 1, probably at about cone 2; no cone number 2 was put in the test, as the temperature required for fusion of the unknown mixture was a complete surprise. Even when it went down, it made merely a nice white porcelain, and indicated that it was some distance from liquidity.

This single test at once dispelled any hopes of being able to utilize bone as a vigorous aid in low temperature work. It did not shatter our hopes of being able to still utilize glass alone, which we next prepared as follows:

TABLE I.

No.	Ingredients	Molecular Formula			
		Na_2O	CaO	Al_2O_3	SiO_2
1-B	Glass alone	0.5	0.5	0.0	2.50
1-C	Glass + 0.1 clay	0.5	0.5	0.1	2.70
1-D	Glass + 0.2 clay	0.5	0.5	0.2	2.90
1-E	Glass + 0.3 clay	0.5	0.5	0.3	3.10
1-F	Glass + 0.4 clay	0.5	0.5	0.4	3.30
1-G	Glass + 0.5 clay	0.5	0.5	0.5	3.50

These mixtures were each prepared, mixed with dextrine, molded into cones, dried, and tested against cones 010 to 1 as before. To our great surprise, No. 1-B, consisting of pure glass alone, stood up till cone 03 was down flat, and cone 02 was bent to a semi-circle, point touching. At the same time, mixtures 1-C and1-D were almost as much affected as 1-B, while 1-E was slightly bent and F and G were not yet affected. This showed that the melting point of common glass, if fairly represented by our sample, was altogether too high for our purpose, and also that a cone in which glass was the principal part, constituting 70 per cent. or more of the mixture, melted substantially as if it were pure glass. It requires more than 30 per cent. sterile or infusible matter to sensibly reduce the melting of the glass mixture.

This second test established the fact that no help was to be expected from common glass as a flux, at temperatures much below where feldspar becomes available, which completely removes it from the list of available supplies for our purpose. This fact is directly contrary to our previous comparisons, and indeed the idea seems general among ceramists that common glass is a valuable aid as a flux, where feldspar and Cornwall stone are too hard, and where lead is not desired. The writer is personally familiar with several cases where attempts have been made to use it in stoneware glazes, or as a body flux, but in every case with similarly disappointing results.

A comparison of the formulae of the two substances shows us that there is no chemical reason for expecting to derive any great advantage from the glass, viz.:

Feldspar ..... K_2O, Al_2O_3, 6 SiO_2.
Common glass.. Na_2O, CaO, 5 SiO_2.

and the results are therefore reasonable, though contrary to the general impression.

IV. Influence of Changes in Total Acidity, Maintaining $Na_2O : CaO :: 1 : 1$.

The query now arose as to whether common glass represents the most fusible silicate which can be made from the ingredients of which it is composed, viz., Na_2O, CaO and SiO_2. Seger has stated that the glass-maker must remain between the ratios RO, 2 SiO_2 and RO, 3 SiO_2, because the glass becomes too fluid below the former, and too pasty above the latter extreme. To test this matter, the following series was devised:

TABLE II.

No. of Glass.	Molecular Composition.			Oxygen Ratio Base : Acid.
	Na_2O	CaO	SiO_2	
1-H	0.5	0.5	2.50	1 : 5
1-I	0.5	0.5	2.00	1 : 4
1-J	0.5	0.5	1.50	1 : 3
1-K	0.5	0.5	1.00	1 : 2
1-L	0.5	0.5	0.75	1 : 1.5
1-M	0.5	0.5	0.50	1 : 1

These glasses were prepared by mixing two batches, 1-H and 1-M. 1-H consisted of 53 parts of common soda ash (Na_2CO_3), 50 parts of Paris white, 150 parts of potter's flint, all of which were ground intimately together in a dry ball mill. No. 1-M consisted of the same quantities of soda and lime, with only 30 parts of flint. From these two extremes, the other four glass batches were prepared by blending:

No. 1-I=3 parts, 1-H and 1 part 1-M.
No. 1-J=2 parts, 1-H and 2 parts 1-M.
No. 1-K=1 part, 1-H and 3 parts 1-M.
No. 1-L=1 part, 1-H and 7 parts 1-M.

Each batch was weighed, mixed thoroughly by hand, put two or three times through a sieve, to prevent lumps of any ingredient forming, and finally put into a large white-granite coffee cup, which served as crucible for the melt. The cups were all placed in an up-draft kiln, and fired to cone 8. No covers were used, so that the behavior of the glasses during fusion could be observed. None of them swelled up much, or foamed in fusion; not one overflowed its cup.

After cooling the kiln, the cups were removed, broken, the glass cracked out in large or small pieces, and carefully sorted to remove all particles of the walls of the cup, which shivered in cooling and adhered to the glass. This was a tedious task, and took about 1½ or 2 hours per sample The clean glass was then crushed to sand, and pulverised in a mortar, until it passed through a 100 mesh screen, dry, when it was put into bottles and labeled. The process could have been somewhat hastened by removing the cups from the kiln hot, and pouring the fluid glass into water, and thus crackling it, but it was though better to cool slowly, in order to procure and preserve a sample of each glass or slag for future reference.

The silicates produced in this series were by no means uniform in appearance.

No. 1-H—Common window glass formula.

This was a fairly-well fused, light colored glass, full of a multitude of very minute bubbles which the glass was too

viscous to disengage. Evidently, cone 8 is too low a temperature to permit this glass to become very fluid or thin.

No. 1-I — Representing Seger's glass of minimum acidity.

This was a clear brilliant glass, almost perfectly free from bubbles of enclosed gases. Color same as before. No crystals or segregations were found.

No. 1-J—This and subsequent silicates are below the ratio prescribed by Seger.

This silicate was still a clear, transparent, light colored glass, free from bubbles of enclosed gases. It showed on its surface a number of large white crystals of the Isometric system, some of them as much as $\frac{1}{8}$ of an inch across, and extending down into the glass $\frac{1}{16}$ from the upper surface. The matrix surrounding the crystals was perfect glass.

No. 1-K—This silicate was an almost opaque, greenish white slag, of vitreous surface and fracture. It had changed very much indeed from the preceeding, and looked as if it were wholly composed of the same silicate which composed the white crystals found on the surface of 1-J.

No. 1-L—This was a slate gray, opaque, vitreous silicate; hard, but could be cut with a good knife. It gave evidence of crysralline structure when examined closely, but appeared otherwise like a stone. There were more or less bubbles in it, but the mass was not strongly vesicular. Its appearance suggested that it had been well fused, but not that it had been notably fluid.

No. 1-M—This is a rough, coarsely vesicular, silicate, composed of various colors—gray and bright sky-blue predominating. It appears wholly stony at first sight, but on close examination, is seen to be a mass of crystalline matter, some of the crystals being clearly distinguished by the unaided eye. It was not apparently well fused, and was the only one of the series giving evidence of too little fusion. The colors are distributed irregularly, and the blue is a prominent factor in it. What this mineral is, cannot be even guessed, but it seems evident that the amount of silica present is too small to actively engage all of the Na_2O and the CaO, and hence several compounds, of quite diverse

character, have been formed and are mingled in the slag.

Nothing conclusive could be determined from the appearance of the melts as to their relative fusibility, so the following test was undertaken:

From these glasses, after powdering as described before, cones were made by mixing the glass dust with dextrine paste and molding, as usual, in steel molds. The mixture had neither plasticity nor strength, until dry, but when once dried out the cones were tough and could be handled with ease and safety. Two sets of these were placed on slabs of clay, as usual in cone tests, and put into a double-deck updraft muffle kiln and fired. The kiln was provided with a Chatelier thermocouple, and galvanometer, and temperatures were carefully noted at all critical points. Cones 03, 05, 07 and 09 were also placed in the test. The contents of the lower muffle, being nearer the fire, were first to fuse, and when these cones were down, those in the upper muffle began to go, so that two sets of reading were obtained.

In the lower muffle No. 1-H and No. 1-I were both carried down, and No. 1-J partly down, by a flame striking them for a few minutes, after freshly baiting the fire. This occured early in the burn, and while the general temperature of the kiln was very low, the pyrometer registering only 560 deg. C. The temperature of the flame which carried the cone down was not indiciated by the pyrometer, and is a matter of speculation only. After stopping the flame, and bringing the heat up uniformly, no further change in the glass-cones was produced until Cremer cones 09 and 07 were down and 05 started. At this point, J got completely down, and K followed almost at once.

In the upper muffle, cone 1-I began to go first, followed by J and K. All of these went down partly, before Cremer cone 09 started, but the latter and 07 got down flat, while the glasses were still only bent, Nos. L and M. were unaffected in both muffles,

The test, though not wholly satisfactory, showed that glass 1-I was probably the softest, being distinctly ahead of No. 1-H and somewhat ahead of No. 1-J. The series showed clearly that there was no hope of getting any softer glass

by depressing the acidity below the oxygen ratio 1 : 3 ; in fact, a very marked increase in refractoriness began at once, and the melts showed this by loss of the glassy, and development of the stony, structure.

At the same time, when series III was projected, it was our expectation, based on the statements of Seger, that a marked reduction of the total acidity of the glass would produce exceedingly fusible glasses or slags. It was thought that with such a soda lime-silica compound, it would be desirable to use some Al_2O_3 in the fusion, if possible, both to prevent devitrification and to make a formula in which the Al_2O_3 could be increased from a minimum up to 0.5 equivalents in cone 4:

Without waiting to see the results of series III, and thus proceed in logical order, we attempted to jump at conclusions, with the usual results.

Series IV was formulated as follows:

TABLE III.

No. of Glass.	Molecular Composion.				Oxygen Ratio Base : Acid.	Molecular Ratio $Al_2O_3 : SiO_2$
	Na_2O	CaO	Al_2O_3	SiO_2		
1-N	0.5	0.5	0.00	0.50	1 : 1	1 : ∞
1-O	0.5	0.5	0.10	0.65	1 : 1	1 : 6.5
1-P	0.5	0.5	0.20	0.80	1 : 1	1 : 4.0
1-Q	0.5	0.5	0.30	0.95	1 : 1	1 : 3.1
1-R	0.5	0.5	0.40	1.10	1 : 1	1 : 2.75
1-S	0.5	0.5	0.50	1.25	1 : 1	1 : 2.50

These mixtures were produced as in the preceding case, by blending between extremes.

No. 1-N—Was composed of 53 parts soda ash, 50 parts whiting and 30 parts of flint. No. 1-S was composed of the same quantities of soda and lime, 129.5 kaolin and 15 of flint. The intermediate blends were made in the proportion 4 : 1, 3 : 2, 2 : 3, and 1 : 4 respectively.

On melting at cone 8 as before, and cooling slowly, the melts presented the following appearance:

1-N—Same as 1 M of series III.

1-O—A mark grayish slag, with small sky-blue patches, same color as those in M, distributed irregularly through it;

texture is stony, and somewhat vesicular. No hint of gla s. iness about the specimen.

1-P—A magnificent emerald-green glass, free from inclosed gas bubbles. Surface is a scummy, and a few little segregations of pearly white matter lying on the bottom of the melt.

1-Q—A mixture of green glass like O, with large amounts of pearly white, opal-like segregations, The mass of the two materials is about equal. The opal-like substance may be simply undissolved kaolin, or alumina which has given its silica up to the stronger bases, soda and lime, or it may be some other material, segregated from a homogeneous magma in cooling. The individual particles of it were half as large as peas, surrounded with the matrix of green glass.

1-R—Stony, vesicular slag with no trace of glassiness.

1-S—Ditto.

This series was like-wise tested in cone form in the kiln, in order to see whether any or all of its members were fusi: ble at low temperatures. The test showed that up to temperatures of cone 02, not one of the slag-cones had showed any signs of fusion, while other glasses, more silicious and less aluminous were melting freely around them.

This series does not prove anything directly of service to this investigation, so far as the influence of alumina on the fusiblity is concerned, because neither 1-M nor 1-N were melted, and hence the aluminous and non-aluminous glasses of oxygen ratio 1 : 1 stands in the same position. It does show, however, that the addition of Al_2O_3 does not *increase* the fusibility of the melts materially, at least in compounds already so basic.

Nevertheless, a well known principle is beautifully illustrated in the consequence; *i. e.*, the power of alumina to prevent devitrification.

Melt N, markedly crystalline even to the naked eye, and stony in fracture, becomes crypto-crystalline in O, a perfect glass in P, a glass full of suspended insoluble matter in Q, and a stony mass again in R and S. The amount of Al_2O_3 in the last two numbers of the series was evidently as much too great, as it was too little in N and O.

On the completion of series III, it became evident that it was necessary to learn more in detail the absolute point of greatest fusibility between glasses 1-H and 1-J. Also it seemed desirable to check the results of series III by a confirmatory series. Accordingly series V was designed as follows:

TABLE IV.

No. of Glass	Molecular Composition			Oxygen Ratio Base : Acid
	Na_2O	CaO	SiO_2	
1-T	0.5	0.5	2.50	1 : 5.0
1-U	0.5	0.5	2.25	1 : 4.5
1-V	0.5	0.5	2.00	1 : 4.0
1-W	0.5	0.5	1.75	1 : 3.5
1-X	0.5	0.5	1.50	1 : 3.0

These were made up as before, and blended and melted by a different person, so that no personal errors would be likely to be duplicated. The temperature went to cone 8 as before.

The glasses were in all respects like those of identical constitution in series III. No. 1-X which was a duplicate of No. 1-J, even had the same white isometric crystals on its surface, showing that this was no freak, but a strong and consistent tendency in a silicate mass of this constitution, to split up into definite molecular compounds, one of which happened to be opaque, and thus visible.

On pulverizing and fashioning into cones, and testing in the kiln, the following interesting results were obtained:

TABLE V.

No. of Glass	Composition	Time of Fusion	Temp. Deg. C	Remarks
1-V	RO, 2.00 SiO_2	5:50 P. M.	925	Undoutedly flashed
2-C	RO, 2.00 SiO_2	8:25 P. M.	1075	Fusion normal
1-U	RO, 2.25 SiO_2	8:55 P. M.	1125	.....
1-W	RO, 1.75 SiO_2	.....	.....	Tipped over before fusion took place
1-X	RO, 1.50 SiO_2	8:55 P. M.	1125	
1-T	RO, 2.50 SiO_2	9:05 P. M.	1150	

These results clearly proved that the RO, 2 SiO_2 glass

is distinctly softer than those above it, or well below it, but owing to the incidental loss of 1-W, did not show that the desired minimum did not lie somewhere between RO, 2 SiO_2 and RO, 1.75 SiO_2.

Accordingly the series was again made up and fired, with the following results:

TABLE VI.

No. of Glass.	Composition.	Time of Fusion.	Temp. of Fusion.
1-V	RO, 2.00 SiO_2	6.11 P. M.	1169 deg.
1-W	RO, 1.75 SiO_2	6.11 P. M.	1169 "
1-X	RO, 1.50 SiO_2	6.16 P. M.	1170 "
1 U	RO, 2.25 SiO_2	6.19 P. M.	1192 "
1-T	RO, 2.50 SiO_2	6.25 P. M.	1210 "

The temperatures recorded were much higher in this burn than in the last, but in neither case, were they corrected for atmospheric temperatures outside the kiln, and hence must not be considered as having a close comparative value. They were only used to indicate the relative temperature intervals between fusions, and not the absolute melting points. The scanty time and temperature intervals in this test, probably resulted from injudicious firing at this point, as the rise in temperature was very rapid.

These two burns showed that RO, 2 SiO_2 is at least as soft as any glass of same RO, either more or less acid, and with some presumptive evidence in favor of its being the point of actual minimum.

This fact alone is of great interest and value, and is directly at variance with the ideas which have been generally held on this point. In metallurgy for instance, we have been taught for many years past that most slags find their most fusible ratios between the meta- and ortho-silicates, or between oxygen ratios of 1 : 2 and 1 : 1. And in ceramics, Seger has announced that RO, 2 SiO_2 is the lower extreme of glass composition, because ratios lower than that produce glasses too liquid and too little viscous to work well in glass blowing.

But here we have a glass, whose melting point is lower at an oxygen ratio of 1 : 4, than at 1 : 3 or 1 : 2 or 1 : 1

Seger's statement must have been based on the fact that a softer glass was obtained by each successive diminution of acid down to this point, and without pushing his tests further to see that he was then at the point of maximum fusibility.

Variations in Lime-Soda Ratio.

Having established the degree of acidity at which this RO combination (0.5 Na_2O 0.5 CaO), is most fusible, and having found it so little suitable to the needs of the situation, the next line of attack was through the variation of the RO elements. It was known in a general way that the silicates of soda alone were much more fusible than those of lime. The point to determine, then, was, was whether increase of Na_2O and decrease of CaO in this RO, 2 SiO_2 ,would materially depress its melting point. To develop this information the following series No. VI was made:

TABLE VII.

No. of Glass.	Molecular Composition.			Appearance after fusion at cone 10.
	Na_2O	CaO	SiO_2	
1-Y	1.00	0.00	2.00	Clear, greenish-yellow, can be cut with knife.
1-Z	0.85	0.15	2.00	Clear,bluish color-harder than Y
2-A	0.70	0 30	2.00	Clear, bluish glass, full hardness.
2-B	0.60	0.40	2.00	Clear, bluish glass.
2-C	0.50	0.50	2.00	Lighter color, more gas bubbles in it.
2-D	0.25	0.75	2.00	Semi-translucent, bluish white glass.
2-E	0.00	1.00	2.00	Porous, white solid; vitrified only on exterior parts, where heat was highest.

There was a very marked difference in time of fusion of the members of this series. The high-soda glasses melted very early and quietly, while the high lime end either did not melt at all, or melted slowly. Obviously, no help can come from 2-C, 2-D, or 2-E. In view of the fact that the increase of the alkali in the glass is at the expense of its stability before the attacks of water and other solvents, it seemed clear that a limit in this case would be found from

this cause, if no other. It was argued that if a glass cannot resist the attacks of water, how can we expect it to resist the solvent and distructive action of acid dew in water-smoking kilns, or of SO_3, at temperatures between 300 and 900 deg. C.

To determine this matter of solubility with sufficient exactitude for the scope of this enquiry, one gram of each glass, previously powdered and put through a 100 mesh screen, was treated with 50 c.cs of distilled water, on a water bath for 10 hours with frequent stirring. Finally the liquids were filtered, and the filters washed with hot water in equal amount. The clear solutions were then evaporated to dryness in tared vessels, and the weights of solid residue determined.

The figures are as follows:

TABLE VIII.

No. of Glass.	Molecular Formula.	Per cent dissolved in hot water.
1-Y	1.00 Na_2O, 0.00 CaO 2 SiO_2	100.00
1-Z	0.85 Na_2O, 0.15 CaO 2 SiO_2	24.56
2-A	0.70 Na_2O, 0.30 CaO 2 SiO_2	9.88
2-B	0.60 Na_2O, 0.40 CaO 2 SiO_2	4.43
2-C	0.50 Na_2O, 0.50 CaO 2 SiO_2	4.21
2-D	0.75 Na_2O, 0.25 CaO 2 SiO_2	4.15
2-E	0.00 Na_2O, 1.00 CaO 2 SiO_2	not determined.

These figures clearly show that No. 2-B represents the maximum soda content which such a glass may have, without material sacrifice of its permanence and stability under the attack of solvents. This point has no definite connection with the behavior of the glasses at high temperatures and in acid gases, which is the conditions they must meet in kiln firing, but it constitutes a basis for distrust of the high-soda glasses, at least.

To ascertain their bearing under kiln conditions the ground glasses were made up into cones as before, and fired with the following results:

TABLE IX.

No. of Glass.	Lower Muffle.		Upper Muffle.	Remarks.
	Time of Fusion.—P. M.	Temp. of Fusion-Deg.	Time of Fusion.—P. M.	
1-Y	5.15	855	Betw'n 6 & 7	
1-Z	Fell over before fusing	....	7:55	
2-A	5.50	925	8:25	Cone 010 melted
2-B	7.45	1040	9:05	at 9.30 P. M. in
2-C	8.25	1075	9:20	upper muffle.
2-D	9.35	1250	did not fuse.	

The soda glass, 1-Y, showed its marked fusibility over any of the others in both upper and lower muffles, but the readings gotten from it were very difficult to interpret, as it did not fuse regularly, but simply softened and swelled until finally it was a spongy fluid. The time periods recorded represent the best judgement that could be formed under the circumstances. In as much as it is one of the faults of the Cremer frit, that it swells and appears to give off gases in fusion, and that it is to avoid this fault, in part, that these experiments have been made, it is evident that glass 1-Y and probably 1-Z must be ruled out for this reason if no other. But the solubility table shows both should be ruled out on those grounds also, and that 2-A is the highest soda glass worth further study.

To get a check on the results just given, as well as to establish the connection between the melting points of series V and VI, another burn was made, in which two cones each of No. 2-A, B, C and No. 1-T-U-V-W-X were placed in one slab. The results are appended:

TABLE X.

No. of Glass	Molecular Composition			Aver'ge Time of Fusion P. M.	Aver'ge Tem. of Fusion deg C
2-A	0.70 Na_2O	0.30 CaO	2.00 SiO_2	4:36	980
2-B	0.60 Na_2O	0.40 CaO	2.00 SiO_2	5:30	1083
2-C	0.50 Na_2O	0.50 CaO	2.00 SiO_2	6:13	1169
1-V	0.50 Na_2O	0.50 CaO	2.00 SiO_2	6:11	1169
1-W	0.50 Na_2O	0.50 CaO	1.75 SiO_2	6:11	1169
1-X	0.50 Na_2O	0.50 CaO	1.50 SiO_2	6:16	1170
1-U	0.50 Na_2O	0.50 CaO	2.25 SiO_2	6:19	1192
1-T	0.50 Na_2O	0.50 CaO	2.50 SiO_2	6:25	1210

Cone 010 was also placed on this slab, and fused at 5.13 P. M., at 1055 deg. C. or about 100 degrees above its schedule temperature. This reading is not corrected, and hence has a relative value only; but it shows by increase of alkali and decrease of lime, it is quite possible to make a soda-lime glass more fusible than cone 010.

The net results of this enquiry now stand:

1st. Using one-half molecule each soda and lime, 2.00 molecules of SiO_2 makes the most fusible glass producible.

2nd Diminishing the lime, and increasing the soda to

$$\left.\begin{matrix}0.7\ Na_2O\\0.3\ CaO\end{matrix}\right\}2.00\ SiO_2$$

the melting point falls from 1169 degrees to 980 in one test and from 1075 to 925 degrees in another, or a net gain of over 150 degrees C.

But owing to doubts about the stability of a glass so high in alkali, it was deemed wiser to use 2-B.

$$\left.\begin{matrix}0.60\ Na_2O\\0.40\ CaO\end{matrix}\right\}2.00\ SiO_2$$

as the basis for further tests.

This glass had melted in the last burn, practically with cone 010—inthe lower muffle a little before, and in the upper muffle, a little after. Now, to use such a glass as the basis of cone 010 would be impossible, as large dilution of the basal frit is necessary in cone making in order to bring about gentle and uniform fusion. At the very least, a glass should melt at 200 deg. C below cone 010, in order to permit of sufficient dilution to make that cone work well.

Hence, it will be seen that glass No. 2-B was far from filling our needs in point of fusibility. At the same time, it must be noted that we had brought the melting point down from cone 02-03 to cone 010-09, by the tests so far prosecuted.

VI The most favorable ratio of Alkalies K_2O : Na_2O.

It was now evident that no compound of soda, lime and silica could be produced of the necessary fusibility, without sacrificing other qualities. The question then arose as to the effect of substitutions from the list of availables given before.

It was first determined to try the effect of substitution

of potash for soda and then, the use of the two alkalies jointly. Accordingly the following series VII glasses were made up.

TABLE XI.

No. of Glass.	Molecular Composition.		
2-T	0.6 K_2O	0.4 CaO	2.00 SiO_2
2-U	0.6 Na_2O	0.4 CaO	2.00 SiO_2
2-F	0.3 K_2O 0.3 Na_2O	0.4 CaO	2.00 SiO_2

These were made up from potassium carbonate (c. p.), soda ash (commercial) whiting, flint; were fused in cups to cone 8, and were then broken, sorted, crushed, put through 100 mesh sieve, and made into cones as before. These were tested along with others, but for the sake of clearness the results are treated separately:

TABLE XII.

No. of Glass.	Composition.	Fusion Data.		
		Lower Muffle.		Upper Muffle.
		Time. P. M.	Temp. Deg C.	Time—P. M.
2-U	Potash-Lime glass	7:00	945	7:22
2-U	Soda-Lime glass	6:50	925	7:26
1-F	Potash-Soda-Lime glass	6:36	890	7:10

Cone 010 fused at 6:56 p. m. in the upper muffle.

It will be noted that longer time, or heat soaking, has caused the potash and soda mixtures to change places in the order of fusibility, while the potash-soda cone melts distinctly lower in each case, than that of either alkali alone.

The point seems clear that the mixture of two alkalies is better than either alone. This point is well known in other connections, viz., in fluxing in platinum crucible in the chemical laboratory, and in making slags in furnaces and in substituting other bases for lead oxide in glazes, etc., etc. But so many contradictions had been met so far since undertaking this work, that it was thought best to take nothing for granted, and to prove each point as we came to it.

VII. Resort to Other Bases Than Lime.

The reduction in fusing temperature from all preceding causes was too little, however, to materially affect the problem. Hence, a new series, No. VIII, was perfected as follows:

TABLE XIII.

No of Glass.	Molecular Composition.				Mixture.
	K_2O	Na_2O	RO	SiO_2	
2-F	0.3	0.3	0.4 CaO	2.00	The K_2CO_3, Na_2CO_3 and SiO_2 were ground together in dry ball mill, and then to equiv. parts of this mixture, the respective oxides, or carbonates were added.
2-G	0.3	0.3	0.4 MgO	2.00	
2-H	0.3	0.3	0.4 BaO	2.00	
2-I	0.3	0.3	0.4 ZnO	2.00	

The glasses resulting from this fusion were all of excellent quality. The calcium glass was the least brilliant of the lot, and the zinc and barium glasses were of especially high refractive index and therefore brilliant to the eye. In fusion, the barium glass fused first, and the calcium glass last, but this could not be accepted as evidence of the fusibility of the glasses when once formed, though of course it gives us a basis for expectation.

On putting these through the usual procedure of grinding, fusion, sorting, regrinding, cone molding and firing, the following figures were gotten:

TABLE XIV.

No of Glass.	Composition.	Fusion Data.		
		Lower Muffle.		Upper Muffle.
		Time. P. M.	Temp. Deg. C.	Time—P. M.
2-F	Lime-Glass	6:36	890	7:10
2-G	Magnesia-Glass.	4:42	755	6:30
2-H	Barium-Glass	6:29	880	7:16
2-I	Zinc-Glass	4:42	755	6:12

These figures alone fail to accurately represent the facts, because the fusion of a glass is often a slow process, and a cone may begin to soften and bend a long time before it

actually fuses, and uncertainly arises as to which may be fairly considered having fused.

For instance, in the above case, the Barium glass 2-H, softened at 2:55 p. m., and bent to a perfect semi-circle, apex touching the level of the base. This was done during a sudden flash of flame, and while the average temperature of the muffle was below 600 deg. C. However, the other cones had the same exposure as the Barium glass and did not show any signs of fusion, while both of the Barium cones, one in the front row nearest the flame, and the other in the rear row, farthest from the flame, went down as described with only one minute's interval. Having gone down in this decided manner, and clearly given notice of some sort of molecular change, they stood in the arched form without further softening, until 6:29 p. m. when they collapsed. During this time the magnesium glass softened at 3:19 p. m., and fused at 4:42 p. m.; and the zinc glass softened at 4:15 p. m., and fused at 4:42 p. m. The calcium glass did no begin to fuse till 6:34 p. m., and was down flat at 6:36 p. m.

This evidence is undoubtedly somewhat confusing. The only thing which is beyond doubt is that the glass

$$\left.\begin{matrix} 0.3\ K_2O \\ 0.3\ Na_2O \\ 0.4\ CaO \end{matrix}\right\} 2\ SiO_2$$

is the least fusible of any of the four under test. The Barium may be considered as being the softest or next to the hardest, according as the first softening or final fusion is considered the more important,

In the upper muffle, the evidence was less doubtful. The zinc cone was here distinctly first down, followed by the magnesia cone, then Barium and lime respectively.

The situation was now improved to the extent that three bases had been tested, and all made glasses notably softer than lime glasses of the same proportions. Of these, the zinc and magnesia glass were beyond all question much softer than cone 010, and the Barium glass either much softer or about as soft as cone 010.

Without waiting to carry the further comparison of these glasses to its final conclusion, it was thought best to push on

and see if any further notable reductions in temperature of fusion could be gotten by making still more complex glasses, using two or more of the bases together. It was thought that even after sufficiently fusible glasses were found, that there were other problems to be considered in adopting one for final use as the base of a cone series, and therefore it would pay to run over the ground tentatively and find what general combinations gave the greatest promise of developing the required combination of properties.

Accordingly series IX was formulated as follows:

TABLE XV.

No. of Glass	Molecular Composition.						
	K_2O	Na_2O	CaO	MgO	BaO	ZnO	SiO_2
2-J	0.3	0.3	0.2	0.2	....	....	2.00
2-K	0.3	0.3	0.2	....	0.2	....	2.00
2-L	0.3	0.3	0.2	....	....	0.2	2.00
2-M	0.3	0.3	....	0.2	0.2	....	2.00
2-N	0.3	0.3	....	0.2	....	0.2	2.00
2-O	0.3	0.3	....	....	0.2	0.2	2.00

In this series, the K_2O, Na_2O and SiO_2 were weighed out and ground intimately together as one batch, and then divided into small portions, into the which proper quantities of the two remaining oxides were then added and ground in.

The melts resulting were all clear brilliant, handsome glasses, any of which seemed perfectly suited to the usual uses. Those in which barium and zinc were used were brighter than the others, perhaps. The first attempt to make this series was a failure, on account of two defects. First, the glasses foamed and boiled over in fusion, so that but little of some of the melts remained. Second, the wind being high, considerable quantity of iron rust was disengaged from the stack, and got down into the kiln, and into the glass crucibles. Accordingly, the entire series was prepared again, and melted, this time successfully.

It was noted in watching the glasses fusing, that 2-M was considerably in advance of any other in fusing. It was the first to begin to raise from the expulsion of gases, and the first to settle back and begin to clarify. This seemed

significant to us, and led us to expect an equally marked fusibility when the glass was tested in cone form.

The glasses were then pulverized, and made into cones as before, and tested with the results set forth in the succeeding table:

TABLE XVI.

No. of Glass	Variable Elements	Lower Muffle		Upper Muffle	Remarks
		Time of Fusion p. m.	Temp. of Fusion deg.	Time of Fusion p. m.	
2-J	CaO, MgO	5:35	755	*	Undoubtedly less fusible than the other glasses
2-K	CaO, BaO	5:55	800	*	
2-L	CaO, ZnO	5:45	780	6:38	Began latest to fuse
2-M	MgO, BaO	5:20	705	6:39	Bloated in both cases
2-N	MgO, ZnO	5:35	755	6:38	Fused well, did not swell
2-O	BaO, ZnO	4:45	575	6:28	Fused well and regularly

Cone 010, Cremer Series, fused at 7:22 p. m., at 945°C.

Only one feature is salient in the preceding table and that is: None of the glasses containing calcium fuse as readily as those in which it is absent. This agrees with the finding of Series VIII, in which calcium formed the least fusible glass. In this last series, the calcium seems to handicap the mixture in which it occurs, very markedly, even when linked with barium which is supposed to have such strong fluxing powers.

The rest of the series are difficult to fairly evaluate. The barium-zinc glass seemed to fuse first in both muffles; but it was not earlier to start than the barium-magnesia glass. It finished earlier, because the latter swelled and bloated before fusion was complete, and thus obscured its end-reaction.

The series also seemed to show that a distinct reduction in fusion point could be produced by using 0.2 equivalents of two fluxes, rather than 0.4 of any one. This is in accord with the general prevailing idea, and with what was specifically proven in regard to K and Na.

Another significant feature of this burn was the fact that the cones in the upper muffle had far less time interval than

** 2-J and 2-K did not fuse in upper muffle.

the same cones below. The lower cones were fused after a shorter, sharper fire; the upper cones had a longer exposure to sulphuric kiln gases, and this seemed to have had an effect in diminishing the natural difference between them.

To still further probe the matter of the effect of mixture of RO elements, another series, No. X, was prepared as follows:

TABLE XVII.

No. of Glass	Molecular Composition						
	Na_2O	K_2O	CaO	MgO	BaO	ZnO	SiO_2
2-P	0.3	0.3	0.13	0.13	0.13	....	2.00
2-Q	0.3	0.3	0.13	0.13	....	0.13	2.00
2-R	0.3	0.3	....	0.13	0.13	0.13	2.00
2-S	0.3	0.3	0.10	0.10	0.10	0.10	2.00

On fusion, these produced handsome brilliant glasses of high refractive index. Especially noteworthy was 2-R, which had a delicate bluish cast and a beautiful, limpid, yet brilliant appearance. On making into cones and testing, they showed as follows:

TABLE XVIII.

No. of Glass	Fusion Began		Fusion Completed		Remarks
	Time p. m.	Temp. deg. C.	Time p. m.	Temp. deg.	
2-P	4:14	725	4:21	735	A very satisfactory test. No swelling or failure to bend properly.
2-Q	4:14	725	4:37	795	
2-R	4:14	725	4:30	775	
2-S	4:08	700	4:26	755	
Cone 010	5:10	880	5:16	910	

These results seem perfectly decided, and unimpeachable, whatever we may think of their rationality.

In order, now, to correlate the last three series, it was decided to select the three softest glasses from each series and melt them all at once on one slab. This was done with the following results:

TABLE XIX.

No of Glass	Variable Element	Fusion Data				Remarks
		Fus'n Began		Fus'n Ended.		
		Time p. m.	Temp. deg.	Time p. m.	Temp. deg.	
2-G	MgO	5:22	670	5:50	720	Swelled.
2-I	ZnO	5:22	670	6:00	755	Did not swell.
2-M	MgO, BaO	5:14	650	5:40	700	Swelled badly.
2-N	MgO, ZnO	5:40	700	....	....	Swelled.
2-O	BaO, ZnO	5:14	650	5:22	....	Swelled.
2-P	CaO, MgO, BaO	5:14	655	5:40	700	
2-Q	CaO, MgO, ZnO	5:43	705	6:00	755	Swelled little.
2-R	MgO, BaO, ZnO	5:43	705	5:50	720	Swelled.
2-S	{ CaO, MgO, BaO ZnO }	5:43	705	5:50	720	Swelled.
No. 010	Cremer Cone.	6:25	865	6:39	925	

This series of results was exceedingly unsatisfactory and was probably due, at least in part, to an experiment. It had been noticed in all the cones composing Series VIII, IX and X, that is, those in which MgO, BaO, and ZnO partly or wholly replaced CaO, that a tendency was evinced to swell up in fusing, and instead of proceeding at once to clean-cut fusion, to form a puffy mass in which no definite end reaction could be gotten.

VIII, Efforts to Locate Cause of Bloating.

This swelling must of course be ascribed to the liberation of some gas in the process of fusion. What gas it can be is a question more easily asked than answered. The first thought was sulphur, that "bete noir" of all ceramic operations. But, as the glasses were perfectly clear after fusion, and showed no sign of crystalline segregations, such as sulphates often cause, it was thought that they must have absorbed it during the cone burn, rather than while the glass itself was being fused in the beginning. This idea was strongly supported by the fact that where cones were fired in both the lower and upper muffles, the latter always showed less time interval between the glasses than below. This would be the case if they had been sulphured a little, as the infusible crust forming on the out side, would cause the cone to stand with but little progress until finally the shell wonld

fuse and let the fluid contents very rapidly assume a level state. This reaction was repeatedly witnessed, and yet was markedly absent in some of the cones.

Acting on the hypothesis of absorption of SO_3 from the kiln gases, it was thought that if the cones could be introduced into the kiln after the latter had reached 550°C, or visible red heat, that the long delay in getting started would be avoided, and the glasses would fuse before they had an opportunity to absorb much sulphur. Accordingly the kiln was heated up to redness, and the cone slab was introduced, well dried and heated to 150°C on a hot iron plate. This was neatly done and the pyrometer showed the presence of the comparatively cold slab near it, as follows:

	Temp. deg.	Time p. m.
Before slab was introduced.....	615	4:15
Slab put in.....	560	4:17
	590	4:22
	600	4:27
Slab caught up with kiln here.....	615	4:31

The results of this maneuver were anything but conconvincing however, as the cones bloated in greater number and in greater amount than any preceding test. It seems evident that the SO_3 or whatever gas it may be which is causing this difficulty, is a part of the glass, and indeed that slow fusion or slow pre-heating rather favors than hinders its escape.

The results attained were very meager and uncertain on account of the bloating. It seemed tolerably evident that 2-M, 2-O and 2-P, were the three most fusible glasses in the test, though 2-G and 2-I are close behind them. 2-R, 2-S and 2-Q were distinctly less fusible, 2-Q probably the least fusible of any tested on the slab.

In order to test the reverse treatment as to absorption of SO_3, another set of the same cones was mounted on a slab, in the same relative positions, and fired. This time the cones stood in the open kiln $5\frac{1}{2}$ hours before they began to soften. The kiln gases were maintained oxydizing throughout. The results were very much better in every way. The glasses did not swell, and bent gently over till they formed arches, which then collapsed into a puddle, after a little delay.

The results of this burn were as follows:

2-M, 2-O and 2-P were again the softest glasses, closely followed by 2-G and 2-I. 2-R and 2-S showed better in this test, though still behind those named before, and 2-Q was again definitely the hardest glass in the lot. The results exactly check those of the preceding test, though much more satisfactory in execution.

IX. Summary of Results to this Point

The work accomplished up to this point may be summarized as follows:

It has been shown, (A) by reduction of SiO_2 from 2.50 to 2.00 molecules, (B) by increase of alkali from 0.5 to 0.6 molecules, (C) by use of 0.3 K_2O and 0.3 Na_2O, in place of 0.6 of either alone, (D) by replacement of CaO, either wholly or very largely, with MgO, BaO or ZnO or mixtures of these, that a large variety of glasses have been produced which soften at about 650 degrees, and melt at 750 degrees, while Cremer cones 010 placed in the same test, melt from 875 to 925 degrees. Common window glass required in another burn, cone 02, before fusion, in which the pyrometer showed the abnormally high temperature of 1155 degrees. It is not likely that the figures are strictly comparable, but at least, there is no doubt that the glasses produced at the close, melted fully 350 degrees, and possibly 400 degrees below the common window glass first tested.

This statement shows in a word, that real, solid, progress has been made. We have now, not one, but many glasses, any of which fuse 150 to 200 degrees below cone 010, and so far as mere fusibility is concerned, could be used as the basis of a cone 010 mixture. Also, the progress has been attained without recourse to any but non-reducible oxides, as originally planned.

By no means all the work has been yet accomplished, however.

(E) The most fusible members of these preceding glasses has not yet been isolated, and the behavior of most of them has been contradictory and misleading in some one of these tests. It seems assured that Barium will be a constit-

uent of the softest glass, but beyond this we cannot now say.

(F) We do not know the cause of the swelling of these glasses when fired as cones. Whatever the cause, if it cannot be overcome, it will go a long ways towards spoiling the glasses for use as the basis of a cone series. The Cremer frit has this fault, and it is in part to escape this that this work was begun.

(G) We do not know whether these glasses, any of them, are less volatile under long continued heat than the Cremer frit. Their composition gives us the right to expect them to be, but proof is still lacking.

It seemed unadvisable to proceed with further tests under E, to determine the glass of the greatest absolute fusibility, until we had answers to F and G, for we had no assurance that the most fusible glass might not be the one with the greatest affinity for absorbing gases, and for volatizing its own constituents. It is quite within the possibilities of the case, that a glass may ultimately be selected, which is considerably less fusible than the minimum, but whose stability makes it safer as a base-frit for the cone series.

X. The Ultimate Cause of Swelling During Fusion.

Taking up the consideration of topic F, the attempt was next made to determine the cause of the gaseous evolution, by which the more fusible cones have many of them swelled during fusion. The hypothesis has already been advanced, that sulphur in some form, probably that of alkaline sulphates, is the cause of this trouble. The fact of such great differences in the fusion of cones made from the same powder, and burned within 18 inches of each other, in the upper and lower muffles, and the marked effect of longer or shorter exposures to kiln gases, and the strange fact of the shortest exposure producing the worst swelling, all points towards the absorption of gas during the original fusion of the glasses, which is given out more or less completely during the long roasting which the cones receive in heating up before fusion. This physical structure of the cones is favorable to either absorption or evolution of gases, since the burning out of the dextrine leaves the mass spongy.

To test this theory, four glasses, 2-F, 2-G, 2-H, and 2-I, each containing

$$\left.\begin{matrix}0.3\ Na_2O\\0.3\ K_2O\end{matrix}\right\}2.00\ SiO_2$$

in common, and containing respectively 0.4 equivalents of CaO, MgO, BaO and ZnO, and in addition, some Cremer frit whose formula was substantially

$$\left.\begin{matrix}0.5\ Na_2O\\0.5\ CaO\end{matrix}\right\}\begin{matrix}2.00\ SiO_2\\1.00\ B_2O_3\end{matrix}$$

were thoroughly ground to a fine dust; each was then mixed with an equal weight of pure Florida kaolin. The purpose of the kaolin was to make the mixture spongy, and thus hold the mass open for the absorption or expulsion of gaseous matter during the heating process. The kaolin would dry to a spongy mass, especially after it had been reduced in plasticity by the addition of 50 per cent. of non-plastic glass-dust, and after dehydration, the pore system would be still further developed by the loss of combined water and organic matter. The five different mixtures were then made plastic with water only, and molded into cones, of which each batch made seven.

When these cones had dried, three of each batch were placed in a small gas crucible furnace, about four and one-half inches internal diameter and six inches deep. A small pat of clay had been previously prepared with shallow triangular holes into which the base of the cones would fit, and thus stand erect. This pat had been previously fired, and was set in the center of the furnace, one inch above the floor. The furnace was then fired up, and heated until its walls had become thoroughly red hot, and at a temperature of 1100 or 1200 C. The gas was then turned off, the firing hole closed, the cones placed in the holes in the pat, the lid replaced and the cones allowed to stand for 20 minutes, in an atmosphere averaging 800°C at least, and free from combustion gases. No sulphuric acid or any other gas, other than air, could possibly have access to the cones during this short period of heating. At the end of 20 minutes exposure to full red heat, the cones were removed, cooled, pulverized and carefully analyzed*

*The analyses were by Mr. R. W. Nauss, B. Sc.

ANALYSES OF MIXTURES OF VARIOUS GLASSES AND KAOLIN HEATED IN 20 MINUTES TO REDNESS IN PURE AIR.

TABLE XX.

Elements.	Lime Glass.	Magnesia Glass	Barium Glass	Zinc Glass.	Cremer Frit.
SiO_2	59.40	62.10	51.54	56.32	
Al_2O_3	21.28	23.16	24.24	22.86	
CaO	7.30	0.68	.....	1.04	
MgO	0.07	2.96	0.36	0.20	
BaO	.....	.....	14.02	.....	
ZnO	.....	.....	.....	8.34	
K_2O	5.63	5.54	4.94	5.43	
Na_2O	5.01	4.83	4.13	4.40	
SO_3	0.32	0.20	0.55	0.21	0.082
Loss on Ignition	1.12	0.89	0.87	0.90	
Totals...	100.13	100.36	100.65	99.70	

Three cones of each of the five mixtures were then placed in the muffle kiln, on clay slabs as usual, except that they were exposed in the open kiln, and not protected by the usual covering.

They were brought up to a dull red heat at the rate of 100°C per hour, and were then subjected to a special sulphur treatment as follows:

The heat was advanced 100° at a time, but not by slow and steady gains. On the contrary, the heat was urged up as fast as possible, without flashing, occupying 20, 30 or 40 minutes to rise 100°C. The damper was then shut down tight, limiting the draft to what could escape by leakage. Into the fire, copperas was now thrown in successive doses of five and six ounces at a time, made up into a ball with enough plastic clay to keep it together, and to prevent the evolution of the SO_3 in a momentary cloud. This was continued until the heat had fallen back considerably, when the damper was lifted, and the temperature moved up another 100°C.

By this treatment, the cones were subjected to alternating periods of a still stagnant amosphere, reeking with SO_3 and combustion gases, and an actively circulating atmosphere charged with combustion gases and free air. No

period of reduction of any importance was permitted to occur, so that any SO_3 absorbed by the cones would not be expelled by subsequent treatment.

The copperas was used as follows:

TABLE XXI.

Time Periods.	Temperature Readings °C	Position of Damper.	Feeding of Copperas.
6:00 to 6:50 p. m.	510-610	Open	20 oz. in 4 portions.
6:50 to 7:00 p. m.	610-610	Shut	13 oz. in 2 portions.
7:00 to 7:30 p. m.	610-710	Open	12 oz. in 2 portions.
7:30 to 8:00 p. m.	710-710	Shut	24 oz. in 4 portions.
8:00 to 8:25 p. m.	710-850	Open	None.
8:25 to 9:10 p. m.	850-810	Shut	27 oz. in 5 portions.
9:10 to 10:15 p. m.	810-900	Open	None.
10:15 to 11:05 p. m.	900-875	Shut	42 oz. in 7 portions.
11:05 to 1:00 a. m.	875-1000	Open	None.
1:00 to 7:00 a. m.	1000-0	Shut	13 oz. in 7 portions.

Of the ten pounds of copperas used, about three pounds consisted of anhydrous SO_3. Also, it was calculated that the SO_3 and SO_2 rising from the combustion of the fuel itself, would amount to a very considerably quantity, probably 7.5 pounds, so that 10.5 pounds of SO_3 passed through the kiln during the burn. The chief advantage which was hoped for the use of the copperas, was the evolution of considerable quantities of SO_3 at the times when the draft was stopped; it was thought that that which passed through the kiln rapidly while the damper was up was little likely to strongly attack the glass-kaolin mixture.

Since the cones were liberally dosed with SO_3 at temperatures below the vitrification of their body, and while they were still porous and able to admit it, it was thought that if one glass had a less ability to withstand SO_3 or a greater tendency to lose any of its ingredients by volatilization, it should surely show it by analysis after this treatment. The final temperature reached was 1000°C, which was thought sufficient to assist in volatilization of alkalies, without risk of decomposing sulphates of the bases which might have formed.

On opening the kiln next day, we found the cones all vitrified to flesh-red, stony-hard, bodies, very much alike,

except the Cremer frit cones, which had fused and gone down at 950°C or about where cone 010 should fuse.

These cones were then finely pulverized and their respective contents of sulphuric acid (SO_3) determined.

TABLE XXII.

RESULTS OF SULPHUR TREATMENT.

	Percentage of SO_3 after heating in Pure Air.	Percentage of SO_3 after heating in Kiln Gases.	Increase in SO_3	Percentage increase on Original Amount.
Lime-glass Cone	0.32	0.47	0.15	47
Magnesia-glassCone	0.20	0.295	0.095	47
Barium-glass Cone	0.55	0.70	0.15	27
Zinc-glass Cone	0.213	0.247	0.034	16
Cremer Frit Cone	0.082	0.588	0.506	617

The results of this test are of great interest. The zinc-glass seems to contain as little sulphur as any glass in the lot, and to take up much less than the others, relatively and absolutely. The actual quantity of SO_3 taken up was only about one-third of that of the magnesia-glass, and less than one fourth of the amounts absorbed by the lime- or barium-glass. The magnesia-glass shows a low actual sulphur content, but a rather high percentage rate of absorption. The actual amount absorbed, however, is small.

The lime- and barium-glasses show to a disadvantage from both points of view. They contain larger initial quantities of SO_3, and they absorbed larger quantities in the test. The lime-glass is unsuitable from this basis, then, in addition to the very clear evidences of unsuitability in the fusion trials.

The barium-glass has the advantage over the lime-glass of being more fusible, but its sulphur behavior is worse if anything.

The Cremer frit is the most surprising member of the series. Its extremely low sulphur content in the beginning and its remarkable absorption of SO_3 in the test explain the reason why this glass has given such unsatisfactory results in practice, as the flux for a cone series.

XI. The Relative Volatility of the Glasses.

It was thought that the alkalies would be the elements most readily expelled from the glass-kaolin cones, and that their loss would most rapidly affect the melting point of the glass. Accordingly, the same samples were carefully analyzed in duplicate for their alkalies, with the following results:

TABLE XXIII.

Mixture.	Heated 20 minutes to redness in pure air.			Heat 10 hours to redness in kiln-gases.			Loss or gain.
	K_2O	Na_2O	Total	K_2O	Na_2O	Total	Total
Lime-Glass Cone	5.63	5.01	10.64	5.73	5.18	10.91	+0.27
	5.96	5.18	11.14	5.58	4.78	10.36	—0.78
Magnesia-Glass Cone	5.54	4.83	10.37	5.53	5.15	10.68	+0.31
	5.63	4.50	10.13	5.91	5.16	11.07	+0.94
	.....	.....	.....	5.40	5.11	10.51	.....
Barium-Glass Cone	4.94	4.13	9.07	4.12	3.86	7.98	—1.09
	4.69	4.23	8.92	4.41	4.11	8.52	—0.40
Zinc-Glass Cone	5.43	4.40	9.83	5.54	4.86	10.40	+0.57
	.....	....	.....	.....	.....	.....	.....

It seems difficult to arrive at any clear conception from the above as to what actually takes place in these glasses. The analytical results are very probably somewhat at fault, as the duplicate determinations do not check as they should, in a number of cases. However, the analyses cannot possibly be so far wrong as to account for the main incongruities.

It is evident at least, that there is no characteristic or heavy loss of alkali, by the longer exposure to heat and acid fumes. In fact, the losses by silica and alumina must have been considerable in some cases to make the final content of alkali distinctly higher than in the beginning.

While these figures are not as conclusive as we should like, still they seem to make it reasonably safe to conclude that volatization of alkali is not a serious factor in any of the cases tested, and therefore, presumably, not with any other glasses which the further development of the series might require.

XII. Isolating the Most Favorable Glass.

Referring back to Section IX, we are now ready to attack E once more, and under better circumstance than in the first instance. We have shown, first, that zinc glasses, or magnesia glasses, or magnesia-zinc glasses are least liable to take up sulphur in offensive quantities and that volatility is not a serious fault with these glasses, more than with others.

Hence, the inquiry now narrows down to the consideration of what ratios of ZnO and MgO will give the most fusible and most stable glass.

NOTE.—The work had been carried but little further at the time of publication, and is not yet ready for announcement. It is hoped to make the selection of the best glass, and demonstrate a cone series made from it, in the future.

DISCUSSION.

Professor Charles F. Binns: I would like to ask Professor Orton to tell us what form of the salt he put into the frit in each case?

Professor Orton: I used soda ash, or common commercial carbonate to introduce my Na_2O. I used the laboratory carbonate of potash, but once our supply of the carbonate ran low and we used the nitrate instead. The calcium oxide was derived from pure whiting. The barium was used as a carbonate. The zinc was used as the oxide.

Professor Binns: Was there any connection between the use of the nitrate of potash and excessive boiling or foaming of the glass during fusion?

Professor Orton: I first had trouble from foaming when we used the nitrate, but later, when we used the carbonate, it boiled almost as bad. I was not able to see in the second burn that the carbonate of potash had behaved much better than the nitrate.

Professor Binns: Another question. Is it perfectly clear that all the CO_2 was expelled in the fritting? Is it perfectly clear that none of the swelling could be attributed to CO_2?

Professor Orton: No. I do not think it could. I don't believe you will find any CO_2 in silicates which have attained the condition of clear perfectly fused glasses. I don't be-

lieve it is possible that CO_2 could still remain in solution in the glass. Sodium carbonate decomposes pretty rapidly above 850°C, especially if mixed with silica. Heated to cone 8, as we did with these glasses, you get a perfectlv clear quiet glass, through which you can look down to the bottom of the crucible, as if it were water, instead of molten silicate.

Mr. Stanley G. Burt: I think it possible that all the CO_2 was not driven off in fritting. I have noticed in my experiments, when fritting an alkaline carbonate with silica, you first get an effervesence, and in time the melt gets perfectly clear and quiet, and you can go to an intense white heat without further change. You might imagine the carbonic acid was all gone, but drop the least additional silica in it, and more gas is at once set free. There must be some carbonic acid present to explain that. I would like to ask if you tried prolonged fusion in forming the original frits? I find that rapid fusion enables the surface to fuse, sealing it as it were, and destroying the posibility of the gas escaping. In slow fusion, long before the actual melting sets in, the bulk of the gases escape through the porous mass, and you can go ahead without swelling.

Professor Orton: The mixtures were fused for periods running from eight to twelve hours and were most carefully watched through the fritting stage, when the gases were most rapidly coming off. The mixtures in the cups would settle and shrink for a time, then begin to swell and rise up, and sometimes would extend like a cylindrical plug an inch or more above the edge of the cup. Then they would gradually flatten back, or the crust would cave in, showing the molten interior, and the whole would rapidly settle down to an inch or two of clean glass, as transparent as water.

Now, the evolution of this gas was such a distinct stage and its beginning and ending were so sharply marked that I have regarded it as a definite chemical reaction and have considered it as marking the expulsion of CO_2. The idea of a molten glass of any considerable acidity retaining any CO_2 in it after it has been heated 500°C above its point of visible gas evolution is new to me, and I am free to say it does not seem probable.

Professor Binns: That is a point which could be readily established. You could find it in the frit, if it was there.

Mr. Burt: You spoke of the fact that the cone should be mixed with 70 per cent. of frit, and 30 per cent. of the raw sterile mixture. Aren't these glass cones (pointing at samples) almost entirely frit?

Professor Orton: I did not say that a cone should contain 70 per cent. frit; I said in one case that one which contained 70 per cent. frit melted practically the same as if it were all frit. I said that 70 per cent. frit would not do; we would have to use a larger per cent. of sterile ingredients than 30 per cent.

Mr. Burt: How much sterile material would your best low-fusing frit carry, and still come down at 010?

Prosessor Orton: Fifty per cent. or a little more, I think. That is just a guess.

Mr. Burt: You intend to determine that in further work?

Professor Orton: Yes. I hope to carry this investigation through.

THE CO-EFFICIENT OF EXPANSION OF SILICA.

BY

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The student of Segers laws for body and glaze coefficient is at once struck by a seeming contradiction. He is told first that by increasing the percentage of silica in bodies, he increases his body coefficient, thereby reducing the liability to craze, and then further on he finds that leaving the body constant he may add silica to his glaze, thereby not increasing the glaze coefficient as might be supposed, but on the contrary reducing it. That is, the coefficient of the silica added to the body is greater than the average coefficient of the body ingredients. The final coefficient is therefore raised by adding it, while on the other nand the case is exactly reversed on adding it to a glaze.

I called attention to this in my paper two years ago, and offered as an explanation the fact that while in the body the silica was non-combined, that is free and crystaline, in the glaze it was combined and amorphous. Now while the coefficient of the crystaline silica is high, that of the amorphous is very low; hence we have the increase in the body coefficient, and the decrease in the glaze.

That crystaline silica has a high coefficient is well known. Probably the high expansion of a silica brick is the most striking proof. This coefficient has been accurately measured by Damour, who also measured the coefficient of various bodies showing that one containing 75 per cent. SiO_2 had more than twice the expansion of one showing but 68.4 per cent. So the increase in the body coefficient is readily understood, but what striking proof have we of its low coefficient in glazes?

This point was recalled to my mind on reading an article by Prof. Witte of Berlin, on what he calls an ideal glass. The article was really a discussion as to whether we should consider glass as a liquid or a solid, but the interest

in connection with my subject lay in his description of this wonderful new glass.

A glass, to be ideal, must satisfy many conditions, two of which have eluded all previous experimenters. These two are, *First*, that it have the lowest possible coefficient of expansion, and *Second*, the ability to withstand chemical action. We have all been maddened by breaking lamp chimneys and most of us know about the elaborate experiments to obtain a glass suitable for fine thermometers. The trouble in both cases is due to the high coefficient of expansion.

This expansion must be reduced to a minimum, but what is there from which we can make glass that will give us this low coefficient? The triumph of this discovery belongs to a German. And what does he take? Nothing more nor less than pure silica. He literally fuses pure silica and makes glass of it. Silica fused to a glass is in the amorphous form, and cools too rapidly to crystalize again.

The resulting glass is clear and fine, can be heated to intense white heat without softening, and when at this high heat may be thrown into ice-water without injuring it in the least, simply because of its low coefficient of expansion.

With this test in mind, we readily see how the silica being amorphous in the glaze, the more silica we add to, our glaze (that is, the closer we approach a pure silica glass) the lower our glaze coefficient will be. So Seger's seeming contradiction is explained.

Do these laws agree with the results our practical experience gives us?

Taking first the body, we know that fine grinding of the silica makes a great difference in the results obtained; the finer we grind, the greater the coefficient. However, this does not mean that we have altered the coefficient of the silica, but that we have enabled ourselves to get a better mechanical mix by fine grinding, thereby benefiting in the coefficient of the body as a whole.

In this connection, I may say that of two bodies showing the same percent of free silica, in one the silica merely added as such, while in the other body the clay as found in nature contained the free silica, the latter will have much the higher

coefficient. This, I believe to be due not only to the probable finer grain, but also to the better mix as just explained.

In firing, the body undergoes decided changes in the coefficient. We find that up to fairly complete vitrification, the higher we fire, the greater the coefficient. Mere addition of silica to the body will not raise this coefficient, but each addition of silica necessitates higher fire. That is, if a body maturing at cone 6 crazes, adding silica and still firing to cone 6 won't help matters, because your body is now under-fired. In this case, we consider the craze as being due to our body having too low a coefficient. Now as the body coefficient increases with the fire, an under-fired piece will leave too low a coefficient and craze. Adding flint to the body renders it less fusible, so in order not to have an under-fired body, the firing must be carried on to cone 7 or 8.

If on the other hand a body, which at the proper heat is free from craze, is over-fired, we may find craze setting in again. How does the theory of the two laws cover these practical results?

In the case of the over-fire, the explanation seems simple. Over-firing to the ordinary potter means vitrification of his body. Vitrification means converting the free crystaline silica into silicate formations, a change from high coefficient to low, which is just what we don't want in the body.

By the ordinary potter, I mean one making pottery as distinguished from one making porcelain. The porcelain maker aims for a complete conversion of his free silica and makes up for the resultant low coefficient in the body by using a very high percentage of silica in his glaze, and a consequent low glaze coefficient. My own experience shows the over-fire craze to be very rare.

Now, as for the under-fired ware, the explanation is not so simple. It does not seem probable that a substance without chemical change, would change its coefficient from mere heating. What we do know is that when we grind our silica, and thereby bring about a more intimate union, we greatly increase our coefficient. It seems probable that our increased coefficient from firing is due to the fact that as we

fire, the body contracts, thereby giving a more and more perfect union. That is, a semi-vitrified body will have a greater expansion than the same body, open and highly porous.

Before leaving the consideration of bodies, a point occurs to me which I wish some member fortunate enough to possess a fine microscope would investigate. This point refers to another one of Seger's laws. He tells us that substitution of a ball clay for a kaolin will increase the body coefficient. This is undoubtedly true, but why? Undoubtedly ball clays as a rule carry more free silica than kaolins, but even allowing for this, the result is the same. I believe it is due to the closer union of the particles that I have been speaking about. This closer union in a ball clay is due, first, to the fact that as it is a sedimentary clay, its particles have undergone a very fine natural grind in the waters which carried them, which the kaolin has not, and second, to the fact that the higher per cent of impurities in the ball clays cause it to contract much more readily. It is the question of the relative fineness of the ball clay and the kaolin, that I would like to see investigated with a microscope.

Considering glazes next, we find the same thing true that we found for bodies. That is, on adding silica, we must have additional fire. However, an under-fired glaze is as a rule so self evident, that no potter stops at an under-fired glaze.

It is at times hard to tell an under-fired body, but not as a rule an under-fired glaze.

To test the Seger laws, I made nine identical pieces and divided these into three groups of three each, calling them A, B and C. The A group was given an under-fire, the B a correct fire, and C an over-fire. All were then glazed in a uniform glaze. 1A was then given an under-fire for glost, 2A a correct fire and 3A an over-fire. The same scheme was followed in groups B and C. In this way the field was pretty wellc overed; that is, the field of over- and under-fireing.

On examining my results, the most noticable thing was that a decidedly worse result was obtained from an under-fired glaze than from an under-fired biscuit, though both were bad.

Another interesting point was that the under-fired glaze might have the clearness and brilliancy of one fully fired. That is, between many under-fired glazes, and the same fully fired, a change has taken place hardly noticable to the eye. If, however, we examine the under-fired glaze with a magnifying glass, we discover many small bubbles down in the glaze. The question at once arises if the glaze is fused to clearness, how to explain these bubbles?

If silica is added to a molten solution of Na_2CO_3, the CO_2 is displaced and sodium silicate formed, with the resultant solution less fusible. Now if we heat it higher, and add more SiO_2, more CO_2 will be given off. This we may repeat at a higher heat, and it is surprising at how high a heat CO_2 will still be given off. Each addition of SiO_2 renders the mass more infusible, and working with a blow pipe I was unable to reach a point at which further CO_2 was not given off.

Now in the case of $CaCO_3$ fired alone, we have no fusion and the bulk of the CO_2 passes off at red heat, but could not a considerable per cent of its CO_2 be retained if there was fusion? In making our glazes, we frit our Na_2CO_3 and $CaCO_3$ together with ingredients, such as $B_2(OH)_6$ and PbO, both low fusers, thereby I believe retaining considerable CO_2.

Now I believe the bubbles I spoke of are CO_2. Some claim they are air bubbles, but this cannot be, as you can see them over our vitrified bodies. They are not the miserable SO_2, of which I have spoken before, as these leave no blister after them, merely small not unpleasant pin holes; so I feel sure these are not SO_2.

The fact that the under-fired glaze appeared clear would seem to indicate that the SiO_2 in the glaze mix had gone into a silicate formation. By clear, I mean there was nothing undissolved in suspension. The bubbles of CO_2 still present indicate to my mind the fact that at the heat at which the glaze was fired, there was not sufficient SiO_2 present to displace all the CO_2 which could be displaced at that heat. So the glaze, acting on the body, is dissolving SiO_2 from the body which in turn is displacing CO_2 from the glaze. If now the glaze is held sufficiently long at a uniform heat, we will

presently reach a point at which no more can be displaced for that heat. This is due to the fact that taking up SiO_2 from the body renders the glaze less fusible, therefore less fluid; the movement of the molecules is retarded, and any carbonate directly in contact with the body being decomposed, no fresh carbonate can reach it. If however, the heat be raised, the reaction starts up again, and fresh bubbles are formed, So to free a glaze from these bubbles, it should be held constant at its maximum heat a sufficient length of time. This is just what the majority of potters do. I do not claim that all glazes would noticably show this phenomenon. Many have too low a percentage of carbonate in any form, but I believe the majority do. I have known glazes that could be freed from this defect in no other manner.

A glost kiln cooled too rapidly shows these pin hole pits very badly, due not only to the scars not having had time to heal, but to the fact that slow cooling gives more time for the glaze to free itself as I have explained.

It may seem hard to see just what connection all this has with my subject, but what I aim to show is that while the under-fired glaze crazed, and the correctly fired one did not, this was due to the latter taking up silica from the body. That the glaze so badly under-fired as to have parts unfused should craze so very badly, would indicate that here the silica had as yet not entirely changed to the amorphous form.

At some future time, I hope to speak on the seeming error of what I may call the silica laws when applied to matt glazes.

DISCUSSION.

Mr. Thomas Gray: I would like to ask the cause of over-fired wares crazing.

Mr. Burt: The damage from over-firing is in the body, not the glaze. We want to get the high coefficient of crystalline silica. Over-firing means the conversion of crystalline silica into silicate formations. It is no longer crystalline silica with a high coefficient, but it is an amorphous silicate with a low coefficient.

Mr. Gray: I want to inquire what the statement as to too rapid cooling in the glost kiln means? We draw the fires as soon as done burning, and soft coal cools more rapidly than hard coal. Do you mean cooling more rapidly than with soft coal? I have often wondered whether the pimple indentations were formed by too rapid cooling.

Mr. Burt: There are a great many methods of cooling a kiln. The porcelain manufacturer throws the kiln wide open, and lets in cold air with a rush. That is rapid cooling. In the ordinary pottery works, they seal the glost kiln up. Sometime ago Professor Binns wrote me and asked me what my opinion was as to these pin holes, and I told him what I do you. He asked me what was the remedy, and I said not to cool too rapidly. He went a step further than that, and did not draw his fires, cooled slowly, and was at once freed from the trouble. However, you have got to be careful not to generate a reducing gas by leaving the fires undrawn and sealing up a kiln.

At the Cleveland summer meeting, we took a tour down to Akron; a very interesting trip. As we were going through a stoneware works, they had just fired off a kiln, and a man was sealing up the kiln. Professor Binns asked him what he was sealing that kiln for, and the man answered that if he did not seal the kiln, he would get ware full of pin holes.

Mr. Gray: As soon as we are done firing, we pull the fires right out and sometimes open the test holes half an hour after the fires are drawn. I have not noticed any pimples.

Mr. Burt: What I say in my paper is, that I do not claim all glazes suffer from this difficulty. If your glaze does not happen to suffer, cool as rapidly as you can, but if one of you is unfortunate enough to suffer from this difficulty, then I say your remedy is to cool slowly.

The Chair: I think in view of Mr. Gray's former remarks about matt finish, he might try cooling slowly. Whether that matt surface is pimple or not, will take a microscope to determine.

THE CONSTRUCTION AND EQUIPMENT OF A WHITE WARE POTTERY.

BY

ARTHUR S. WATTS, NEW LEXINGTON, O.

For the past year I have devoted my entire time to the designing and erection of a 12 kiln china ware plant. From my experience along this line, I propose to offer the society my idea of a white ware plant, trusting that it may find some helpful suggestions from a study of my ideas. As I shall publish an outline plan of the buildings, it will be unnecessary to discuss their arrangement here. What I propose is to take up the various defects common in such plants, and offer what I propose as a correction.

While I approve of all practical labor-saving devices, I do not consider any mechanical device a good investment that will not save its cost in one year. We will first look to the power plant, which I will discuss in detail later. In my engine room, will be two engines and two dynamos. One of the latter will be used for power, and the other for light. In the average white ware plant, so little power is used beyond the clay shops, that none is supplied beyond this point. I propose to make use of motors wherever power is needed beyond the bisque kiln shed, as it is quite as economical and saves the long shafting otherwise necessary.

Adjoining my engine room, I propose a thoroughly equipped machine shop, where all work of the factory may be done.

In the clay rooms, the first subject that demands our attention is the material and clay sheds. Many factories have these sheds so located that a long haul is necessary to reach the slip house. I propose to make use of modern conveying machinery, and with a grain shovel inside of the car, I will be enabled to unload a car of material with one man in one-third the ordinary time. I also find that flint

sand can be purchased for about $1.00 per ton, and even with the expense of installing tube or ball mills for grinding, the ground flint can be produced for much less than the market price. The same is the case with feldspar rock. What I propose is to install porcelain-lined tube mills and grind my own flint and spar.

The next practice that I propose to improve upon is the preparation of the body. We must have the body uniformly mixed, if our ware is to be of a uniform color and appearance. The flint and spar ordinarily used are materially coarser than the clay, and hence, especial care must be taken to have them thoroughly mixed. This can not be done in the old fashioned blunger. What I propose is a series of blungers, from which the body passes to a tube mill such as is commonly used for grinding Portland cement. This is the best rapid-grinding apparatus known for clay working, and by careful adjustment the body can be brought from this mill in a perfectly uniform and very fine condition. It has been my experience that this is the only successful means of overcoming cloudiness so common in American porcelain.

From the tube mill, my slip will pass through a trough, where I have installed a battery of horseshoe magnets, charged from my electric lighting line. By this method, I remove any particles of metallic iron that may have stolen into the mixture. I find this a very good thing, since about any factory, annoyance from a few specks of iron in a fine piece of ware is no uncommon occurrence.

The body then passes through the sceern into the deep agitator. I will here explain what I consider an ideal clay slip screen. It is nothing more than a rectangular box 24x30 inches, made of heavy wood to stand jarring. It is set with one end raised about 10°, and the upper end is left open to permit the workings to pass out. The slip is introduced at the lower end. The shaking is produced by having the box supported on four straight steel springs, two at each end. A heavy cog wheel forces the box out of

STRAW SHED
COOPER SHOP
DECORATING DEPARTMENT
PACKING DEPARTMENT
WARE HOUSE
GLOST DRESSING ROOM
GLOST KILN SHED
GLOST PLACING ROOM
DIPPING ROOM
BISQUE WARE HOUSE
BISQUE KILN SHED
BISQUE PLACING ROOM
SAGGER SHOP
GREEN WARE HOUSE
BOILER HOUSE
ENGINE ROOM AND MACHINE SHOP
CLAY CELLARS
SLIP HOUSE
MATERIAL
DEPARTMENT
ELEVATION
PLAN
SCALE

position until a cog can pass under, when the box flies back to its original position, striking either the next cog or a block set for the purpose. This produces a very strong jar, and frees all collected refuse from the surface of the screen, jarring it up the incline until it passes over the top. I have seen this type of screen work for months without needing any repair, and it possesses the advantage of requiring very little height, whereas, the ordinary screen requires from two to three feet of height, necessitating the placing of all blungers very high, and requiring a proportionately higher building.

From the deep agitator the slip goes to the press by means of the pump. If any one machine in a pottery may be considered the "potter's burden," it is the slip pump. Every potter has his own idea of a pump, but mine is a rubber-ball-valve pump. This works by a plunger, but instead of the ordinary brass or leather valve, it has a socket into which fits a rubber ball. This can not possibly get out of the cavity, and when it becomes worn too small, it can be replaced for a few cents, thus giving you practically a new valve. As the rubber takes all the wear, the socket lasts for years This pump gives less trouble where used than any that I have ever tried or seen tried, besides being cheaper than the brass valve commonly used.

Another idea that I have proven to be thoroughly practical, is a pad under each sack on the press. Any slip-house man will tell you that it takes longer to put the last quarter of clay into a leaf than is consumed in pumping up the first three-quarters of the leaf. This is owing to the canvass sack being pressed tight against the iron leaf of the press, leaving no room for the water to run out. By placing a layer of coarse felt or canvas between the sack and the iron leaf, the water can soak out at any ordinary pressure as fast as the pump can force it in. This enables you to pump your press up to 100 pounds without stopping, and you will find that it will take less than one-half the time consumed by the old single sack method. I find further, that a press thus equipped will not burst and run, as the clay

from the broken sack meets the cushion of felt or canvas and clogs, thus enabling the press-man to continue with his pumping, and perhaps use the broken sack the remainder of the day without any trouble. I also find this a great saving in sacks, as no loss is experienced from wear against the iron leaf.

From the press, the clay goes to the cellar. Here is the weak point in most white ware potteries, especially china plants. Ample room must be supplied for aging the body, as otherwise much loss is suffered from cracking. Most clay cellars are too cold. This is the worst condition possible where a bacterial growth is desired, as is the case here. The temperature of a clay cellar should never run below 76°, and an abundance of moisture should be provided. This condition I propose to insure by placing steam pipes next my ceiling. My walls will be lined with heavy oak plank, as will also the floors. The cellar will be of sufficient size that the clay may be aged for two weeks. I find that under proper conditions, a longer period of aging proves detrimental since the clay becomes rotten and full of tiny gas bubbles, which enlarge on burning and disfigure the ware.

The clay shops are on a level with the other floors of the factory, the additional height required being supplied above. This brings the main power shafts on a level with the power shafts of the second floors, except in the room above the slip room, and reduces the amount of belting necessary, while it insures a good dry floor for your slip house. The elevated floor above the slip house is used for a casting room, and no power is required, except for pumping up slip, which is done from below.

The glaze is all ground in ball mills and pumped across to the dipping rooms.

The clay, after aging, is pugged, and goes by means of a belt elevator to the various departments above. The work shop occupies the second floor, and is equipped with oval jollies, etc., reducing hand labor to the minimum. The ware, after being inspected, goes to the green room on the

first floor. This room is divided into four sections; heavy-flat, thin-flat, jollied-hollow, and cast-hollow, enabling the placer to find what he wants without any trouble or delay.

We now come to the placing of the green ware for the bisque kilns. Here the handling of saggers and placing material confronts us. It is customary to place extra saggers about the kiln-shed when not in use, but to this practice I lay much of our dirty ware. It is certain that with a clean, light place for the saggers when not in use, and where the placer may fill the sagger, a much neater and more satisfactory result will be obtained than in a dirty, smoky kiln-shed. I therefor propose a 25 foot room, between the green wareroom and the bisque kiln-shed, where saggers may be stored and filled.

To the subject of kilns, I have given some attention, and while I have not been able to convert others to my views, I am convinced that the center stack down draft kiln is the ideal for white ware, as well as for tile. I can not see the economy or necessity of retaining the old up-draft kiln. Any one who has studied the workings of an up-draft white ware kiln, knows that the outside ring is solid-flat ware, laid in flint or sand, while the center of the kiln consists of hollow ware. Between this and the center, is a great area that is too soft for flat ware, and too hard for hollow ware. The ware taken from this area is never right. Why can we not use a center-stack down-draft kiln, which will give uniform results, and burn only such ware in a kiln as can be all burned at the same temperature? This would necessitate setting an entire kiln of hollow, for every two kilns of flat, but this could be done, as it would mean two kilns of hollow ware, and four kilns of flat ware each week, in a 12 kiln plant. The hollow ware could be burned at a lower cone than the solid-flat ware, and this would produce a product uniform in color and hardness.

The bisque ware goes by a gravity conveyor to the bisque warehouse. Here, I would use power to assist me in removing the sand or flint from the ware. For cleaning all pieces less than three and one-half inches in diameter, such

as creams, butter slips, and small heavy sauce dishes, I use a hickory-lined ball mill filled with sand. The ware is placed in the mill and sand added until it is nearly full. The mill is run until the dishes are clean. The large round ware is cleaned on a wheel. The irregular shapes are cleaned by hand. As soon as the ware is cleaned, it is dusted and placed in tight boxes on wheels, in which it goes to the dipping room adjoining. As the ware is glazed, it is placed in a dryer with doors at both sides, enabling the glost kiln placer to reach the ware without entering the glazing room. This dryer also confines the heat to the glazed ware, and makes a much more agreeable dipping room than we generally find. From the glost kiln, which is also a center-stack down-draft, the ware goes to the cleaning and sorting room, where it is carefully sorted, and such ware as must be decorated, in order to be made saleable, is taken to the decorating warehouse, while the first and second-class ware goes to the glost warehouse. Ware should not be decorated until ordered, and then go directly from the decorating kilns to the packing department, where it is to be wrapped and packed.

Crates and casks for shipping ware will be made on the premises, and brought by gravity conveyor directly into the packing room. Straw for packing will be handled by the same method, hence no quantity of packing material need accumulate in the packing rooms where it might cause a disastrous fire.

Coal for my kilns will be run on an elevated switch, and bottom dump cars being used, no expense will be incurred in unloading. The coal will be distributed about the kilns by means of cars running on overhead tracks and so arranged that the loaded car carries the empty car back.

The sagger shop is so located that the carry to the bisque kilns is the shortest possible.

It has been suggested that my ware houses are small, but actual experience has proven that they are ample to carry a $150,000.00 stock, and I consider that any concern

which accumulates more than that amount of stock must have some cause for being unable to dispose of their product, and should suspend operation until their stock is reduced or the cause of unsalability overcome.

In closing, I desire to remind you that these are simply suggestions, and while they have proven practical wherever I have seen them used, they are open to criticism and would doubtless require changing to suit the location and existing conditions. For a level site and unlimited space, however, I feel that I can assure you that a plant of this description and plan would enable the owner to produce ware at a much lower cost and of a better quality than much that is produced today.

IMPROVEMENTS IN APPARATUS FOR CLAY ANALYSIS.*

BY

EDWARD S. BABCOCK, M. SC. AND CHARLES F. BINNS, M. SC.,
ALFRED, N. Y.

Samples of clay being sent in large numbers to the New York State School at Alfred, for analysis, it has become necessary to devise special apparatus to facilitate the work.

For the preliminary fusion with alkaline carbonates, the blast lamp presents many disadvantages. If worked by foot power it is irregular and exacting, with the frequent result of imperfect decomposition, while a power blower is not always available.

The following is a description of a simple, satisfactory piece of apparatus:

A covered box of sheet iron is prepared, measuring ten inches long by eight inches wide and eight inches high. Three apertures are cut, two in the top measuring two inches and five inches in diameter respectively, and one, two inches in diameter, in the end farther from the larger aperture. All three openings are circular.

The box is filled with plastic sagger clay well mixed with grog. The clay is then excavated horizontally from the lower hole and vertically from the two upper holes in such a manner as to form a tunnel which returns upon itself as shown in figure 1.

A thin vessel of fire-clay is made and burned. The shape is that of a thimble with a broad flange. This is dropped into the upper opening and should hang freely with a space of about one-fourth inch all round. This is shown in position for use in figure 1.

A Bunsen burner is placed opposite the lower hole and a length of stove pipe over the small upper one. For a burner, the bunsen of a Welsbach light answers well, but the orifice should be enlarged to $\frac{1}{16}$ inch.

*Read by title at Boston meeting. Discussion specially invited.

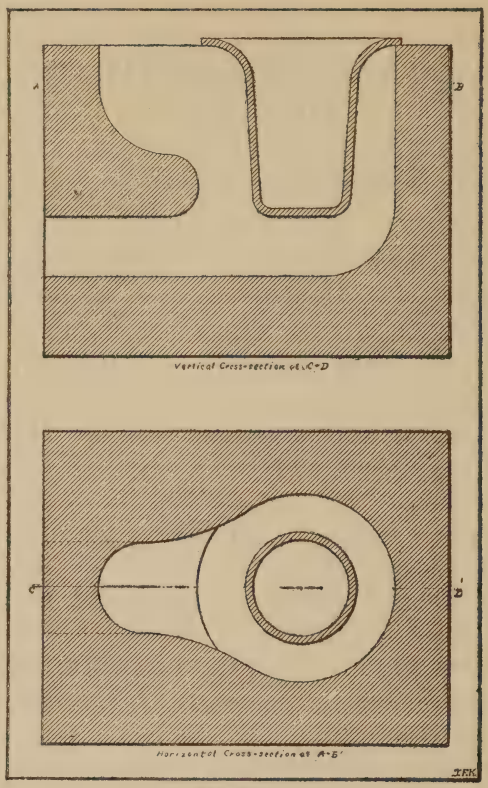


Figure 1.

The platinum crucible with the alkaline mix is set in the clay thimble and will need no attention after the lighting of the gas until a perfect fusion has been secured. Inspection is easy by reason of the wide opening above.

Everyone who has used platinum is aware of the trouble caused by reduction. Particles of metal from surrounding objects, metallic dust from the blower and lamp cling to the platinum and are assimilated, to the speedy destruction of the ware. All this is avoided in the apparatus described, and it is every bit home-made.

A second furnace has also been constructed for the subsidiary operation of alkali determination. Two points in this work are always giving trouble to the analyst, first, volatilization and second, imperfect decomposition.

The method employed is that involving the breaking

down of a clay by ignition with calcium carbonate, known as the J. Lawrence Smith method. A special platinum capsule was procured, measuring 8 centimetres long and 1¾ centimetres wide at the top and 1½ centimetres wide at the bottom. This is fitted with a cover. The furnace is similar to that previously described except, that in place of the large opening at the top, there is a small one in the side below. See figure 2.

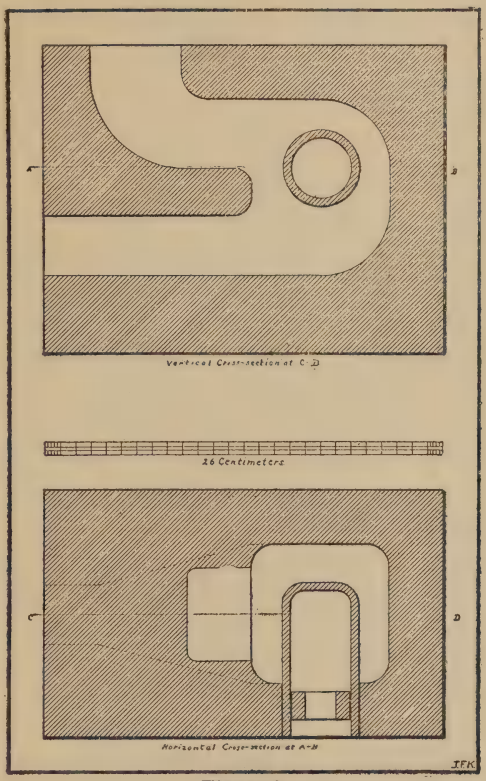


Figure 2.

In this hole a fire-clay tube is inserted, and in the tube the platinum capsule with the calcium mix is set. A long period of ignition can be employed. The cover of the capsule prevents volatilization, and owing to the length of the platinum vessel, the upper end keeps cool enough to condense any vapors without loss.

BACTERIA IN CLAY MIXTURES.

BY

EDWARD C. STOVER, TRENTON, N. J.

For the purpose of testing bacterial inoculation, on Dec. 15, a short vitreous body was mixed, having the following composition:

$$\left.\begin{matrix}0.130\ K_2O \\ 0.052\ CaO\end{matrix}\right\} 1.00\ Al_2O_3 \left\{ 6.26\ SiO_2\right.$$

which figures out as follows:

Clay, 1200,
Flint, 1200,
Spar, 400,
Whiting, 28.

The quantity put up was divided into two equal parts, one of which was mixed with bacteria-laden water, the other with fresh pure water, and both set aside for one month until Jan. 15, when both batches were given to a presser with instructions to make a small baker of each.

The two batches differed much in appearance, the pure one remaining light in color, while the inoculated batch had become quite dark. The latter was tough and plastic and worked without difficulty, while the former was so short it was almost impossible to work it. We could hardly make the presser believe they were both of the same mixture. He declared that the dark colored tough batch was either a different mixture altogether, or had something put into it to make it work better.

This mixture was purposely made without the use of any ball clay to assure its being a short body. Both samples were fired at cone 13, and a glance at them will show clearly which is which, the one made of the inoculated mixture showing a comparatively smooth surface, while the other is full of small rends or tears common to very short bodies.

Both of these bakers were made from the same mould and a slight variation in shrinkage is to be noted, the inoculated mixture showing the greatest shrinkage, which seems

to prove the theory of a closer union of the minute particles in the inoculated mixture than in the one not inoculated.

Potters who are manufacturing porcelain, bone china and other bodies of a short non-plastic nature, could probably make some experiments along this line to their advantage.

DISCUSSION.

Professor Edward Orton Jr.: I will ask Mr. Stover how he prepared the fresh, pure water, and how he knows it was free from bacteria?

Mr. Stover: I took ordinary hydrant water, assuming that is as pure as we could get around any pottery. The foul water was made from a batch of clay, which had been standing for about three months,and was very offensive. The water used for inoculation was a decantation of that mixture. It was very black and very offensive when stirred up. I could guarantee the impurity of that, rather than the purity of the other. In some districts the mixtures of clay are made nine months or a year before making up into ware. The clay becomes quite dark and offensive; and my theory is that it is a bacterial growth which produces this condition.

Professor Orton: Is there anything put into the bodies for bacterial food?

Mr Stover: Nothing, whatever.

Professor Orton: What would you think of putting in a small quantity of starch paste or sugar waste or something of that sort, which would act as a ferment, thus affording food for the bacteria?

Mr. Stover: I think it is a good suggestion. The thing to do is to find out the bacteria which are doing the work and then regularly cultivate them in our mixtures.

Professor Orton: It seems to me probable that the bacterial form which is producing this fermentation and decay is an exceedingly common form, the presence of which we could hardly avoid. It does not seem to me so important to enter into an elaborate microscopic study of the exact species. It seems more important to furnish a proper me-

dium in which they can work. A half or quarter per cent. of decomposible organic matter, would make an enormous difference in the rapidity with which they breed. Ordinary clay does not contain very much food for bacteria.

Mr. Stover: I think the suggestion is a good one, and I will experiment along that line. My object is to reach quickly the same result now obtained by aging clay. Potters generally realize that clay put in a cellar and left awhile, is tougher than when fresh from the bank. Why take two or three months for this result, if it can be reached in three weeks? I will go on along the line suggested, and get further results if possible. It has been shown by others that bacteria flourish best at one hundred degrees Fahrenheit or about that point.

Mr. R. C. Purdy: Is bacterial growth accelerated in a room lined with oak, rather than in a cellar lined with cement?

Mr. Stover: I cannot say. I have not been lining any rooms for the purpose. I have been told that in the manufacture of certain cheeses, which our German friends are very fond of, they must be aged in certain places to get the right result, probably for the proper cultivation of the bacteria.

Professor C. W. Parmelee: Professor Orton suggests the advantage of continuing these experiments along the line of inoculation rather than pure culture. Pure culture might have the advantage of dispensing with the offensive odor Mr. Stover speaks of.

Professor Orton: Mr. Stover's paper last year contained a reference to certain bacilli from one of these cultures, and if I recollect correctly he gave it as Bacillus Sulphureum. It seemed to be one which would be apt to be found in decomposing clay mixtures particularly. They contain more or less pyrites, or other sulphur-bearing ingredients, and these are broken down by the bacteria and sent out as H_2S, which generates a noisome smell. It seems to me we cannot expect to accomplish the work without smell.

Mr. Thomas Gray: I will ask Mr. Stover if he made up

any large amount of these clays (referring to samples accompanying Mr. Stover's note), to know which one had the most loss.

Mr. Stover: No; only these two samples.

Mr. Gray: One, I notice, shrunk in width, and they are about the same length.

Mr. Stover: If broken and placed under the microscope, I think the one inoculated will show somewhat tighter, closer structure than the other.

Mr. Gray: We had some clay which had been mixed for six months, and the man who worked on it said he never had such tough clay and could handle it much better than the freshly mixed clay. I never noticed anything disagreeable about it myself, and did not hear him complain. In handling it, the clay which had aged for six months was very free from cracking.

Mr. Stover: That seems to be along the line of experience of others.

NOTE ON THE FLUXING POWER OF MICA.*

Discussion by Professor Heinrich Ries, PhD.†
Ithica, N. Y.

Mr. Stull's paper on the fluxing effect of mica in ceramic bodies is one that I am sure interests all of us. Mr. Stull comments on the possible reason for muscovite being the common mica in white clays as due to the fact that it closely resembles feldspar in its chemical composition. If we include sedimentary clays in this state, it would seem to me that the absence of the other micas, especially the iron bearing ones, might be because they are so easily decomposed when the clay is attacked by the weather, and therefore in the case of sedimentary deposits it is the more resistant minerals that are left. In the case of residual clays his explanation may be true.

Mr. Stull's results certainly bring out very prettily the effect of fineness on the fluxing power of different ingredients. The larger grains of mica such as are visible to the naked eye in many clays may seem to resist union with the other ingredients of the clay up to a moderately high temperature. I happen to have on my desk at present a whitish clay from New Jersey, which contains a large percentage of white mica particles, any of which would however pass through a 100 mesh sieve. After heating a bricklet of this clay up to cone 8, many of the scales were still easily seen in the middle of the bricklet, although they have lost some of their lustre. At cone 10, those in the interior of the bricklet had nearly all disappeared, although they were still visible on the outside of the bricklet.

The effect of the size of the grain on the fusibility of the clay is a point which has always interested me considerably, and I have recently begun some experiments with different common minerals such as are apt to occur in clay, in order

* Transactions American Ceramic Society, Vol. IV, p. 255.
† Read by title at the Boston meeting, February, 1903.

to satisfy myself on this point, and to find out what fluxing influence the different minerals exert. The common supposition has been that the smaller the fluxing grains, the easier the fusibility of the clay, although in the case of fire clays, Prof. H. O. Hofman considers that this is not the case.

As a first step I made up some mixtures of kaolin with hornblende and kaolin with calcite.

One series contained by weight as follows:

A. Kaolin 25 parts, calcite 25 parts, the latter passing through 150 mesh.

B. Same mixture, the calcite passing through 100 mesh, but resting on 150 mesh.

C. Same as before, but calcite smaller than 80, and larger than 100 mesh.

The object of taking such a large quantity of flux was to have the material melt at a temperature below cone 10 if possible.

A similar series of kaolin and hornblende was mixed up, and these can be designated as A′, B′ and C′.

The results were not unexpected.

At cone 10, A had fused, but not run, B was softening, while C was unaffected.

In the case of the second series similar results were obtained at cone 5.

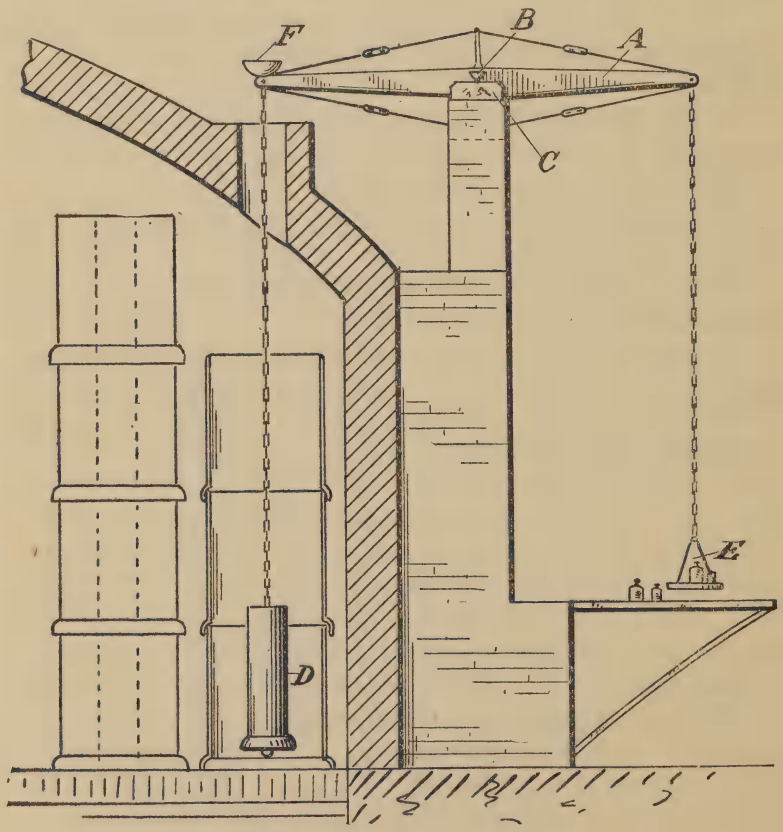
This is simply a preliminary note, and I hope to present some detailed results to the society at the next meeting, after I have carried out the experiments with a number of minerals as well as mixtures.

A GRAPHIC METHOD OF SHOWING LOSS OF WATER IN CLAY BURNING.

BY

WILLIAM H. GORSLINE, ROCHESTER N. Y.

In common with others, we have experienced the disasters attending the too rapid firing of our ware when green, or before the water-smoking process is completed. The idea which led to the adoption of the apparatus employed came from the suggestion of a friend. To describe it would be to compare it to the beam of a chemical balance (see cut.)



But one knife edge (b) is used. This passes through the beam (a) near the center of gravety and extends through each side. On each side of the beam are blocks (c) which rest on the base on the top of the kiln. On the top of these blocks are iron plates to receive the knife edges. The beam is thus allowed to act freely and responds to very slight differences in weight. Suspended at one end, on a line with the knife-edge, is a wire which passes through a hole in a kiln cover. From this wire is hung a trial piece (d) near the floor of the kiln. This trial piece is of the same thickness and degree of dryness as the ware which predominates in the kiln. From a point on the same line at the other end of the beam is hung a counter-weight (e) which is sufficient to bring the beam into equilibrium before the firing begins.

The beam is braced at top and two sides by small cables and turnbuckles. It is made of very dry clear pine instead of metal. For a knife edge, I used an old file ground down to a sharp edge. The foregoing is a brief description of the apparatus used. I have added to it other improvements which it would be difficult to describe in this note, but which would suggest themselves to any one familiar with such work.

As the firing begins and the water-smoking progresses, the mechanical water is expelled from the ware, thus making the latter lighter and causing the end of the beam from which it is hung to rise. Observations are made at intervals, when enough weights are added to a receptical (f) at the end of the beam just above the kiln cover, to restore it to balance.

As is quite clear, the total weights added at any time equal the total weight of the water expelled. Although the results ultimately possible have not yet been secured from these experiments, the point at which the mechanical water has left and the chemical water begins to be expelled, is roughly indicated. The time during which the chemical water is being expelled is unmistakable, on account of the pronounced loss of weight indicated by the apparatus.

In the firing of sewer pipe, we consider this stage of the burning one of the most critical. In fact, as regards the

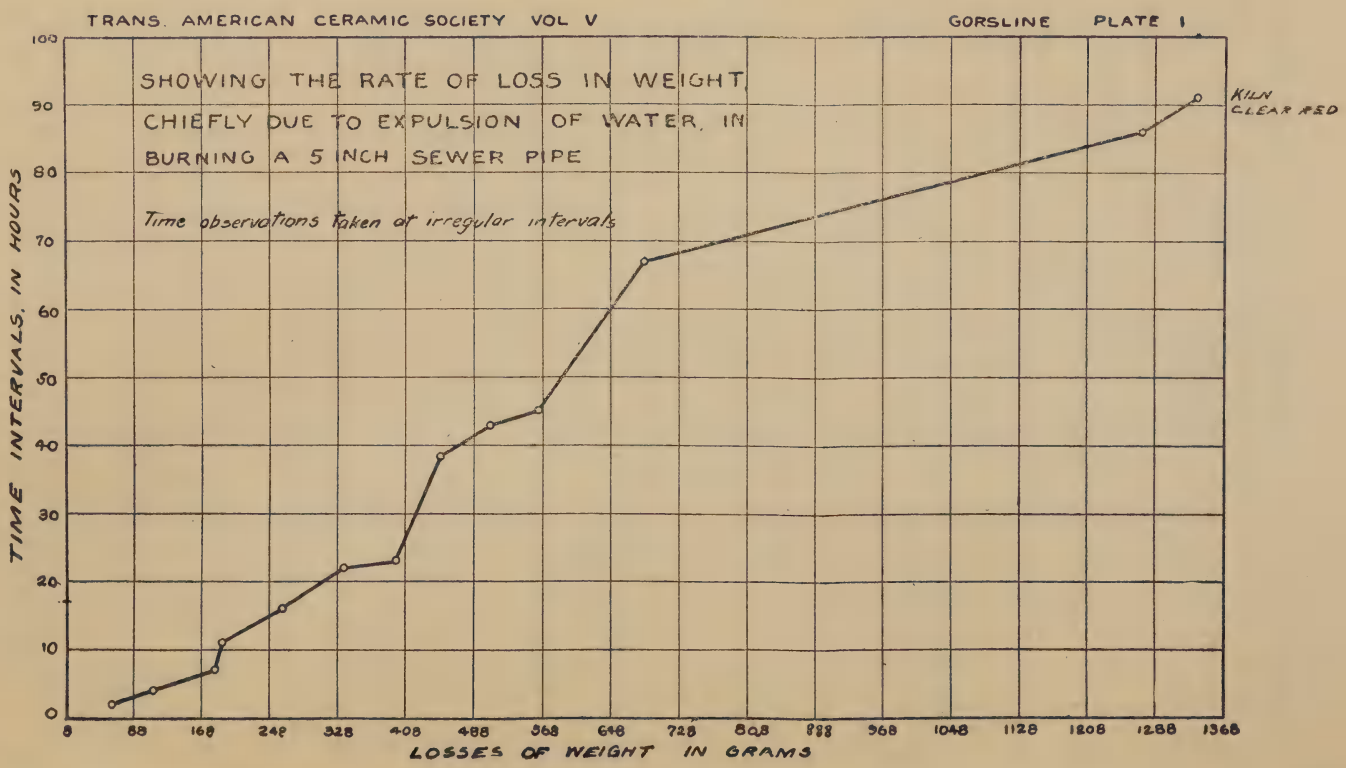
water, it *is* the most critical. It is not common to hear from those burning finer wares, the complaint that when the fire is increased before the ware is sufficiently dry, the ware is injured or ruined by the too rapid expulsion of the water. It may be possible therefore to adapt the principle described above to the burning of fine ware, so that the behavior of the beam may regulate the first part of the burning.

In one experiment, extending from the begining of a firing which occured on a Thursday at 6 P. M. until the kiln was entirely clear on the following Monday at 2:15 P. M., the entire loss of water in a dry five-inch pipe amounted to 1330 grammes. During the first 68 hours, which was up to the beginning of redness, there was a loss of 681 grammes; during the next 24 hours, a loss of 649 grammes, when the kiln was clear. It is thus shown that during the first period the average loss was a little over 10 grammes per hour, during the second period 27 grammes per hour. The difference in favor of the latter, indicates that the chemical water was being expelled during that period. Plate I shows the curve described by such a burn. In another, during 60 hours, the loss was 430. In the first 43 hours to redness, loss 223, in next 17 hours to beginning of clearness, loss 205.

In our regular burning, we use cones one, two, three and four, but number one does not go down until the last day, and, on account of lack of time, in none of these experiments have I taken the temperatures. Nor have we been able, so far, to continue the observations beyond clearness because after that the wires that we used would not withstand the high temperature. It would be possible, however, to continue this measuring of the water expelled, until the beam remained constant, although that might not be reached until the kiln came off.

The total loss indicated is not actually all water, as other losses occur, viz. SO_3, CO_2 etc; but these are not so important as regards weight.

In chart No. 2, the curve is interesting for several reasons. The burners are changed at 6 P. M. and 7 A. M. This curve shows a marked loss beginning soon after the changing of burners one evening. Of course, it is somewhat


TRANS. AMERICAN CERAMIC SOCIETY VOL V
GORSLINE PLATE I
SHOWING THE RATE OF LOSS IN WEIGHT
CHIEFLY DUE TO EXPULSION OF WATER, IN
BURNING A 5 INCH SEWER PIPE
Time observations taken at irregular intervals
KILN CLEARED
TIME INTERVALS, IN HOURS
0
10
20
30
40
50
60
70
80
90
100
0
88
168
248
328
408
488
568
648
728
808
888
968
1048
1128
1208
1288
1368
LOSSES OF WEIGHT IN GRAMS

due to the progress of the firing, but we are confident that it indicated some carelessness on the part of the burner. The irregularity of the curves is, of course, due to the factory conditions, which are not as even and regular as though the burning were conducted in a laboratory.

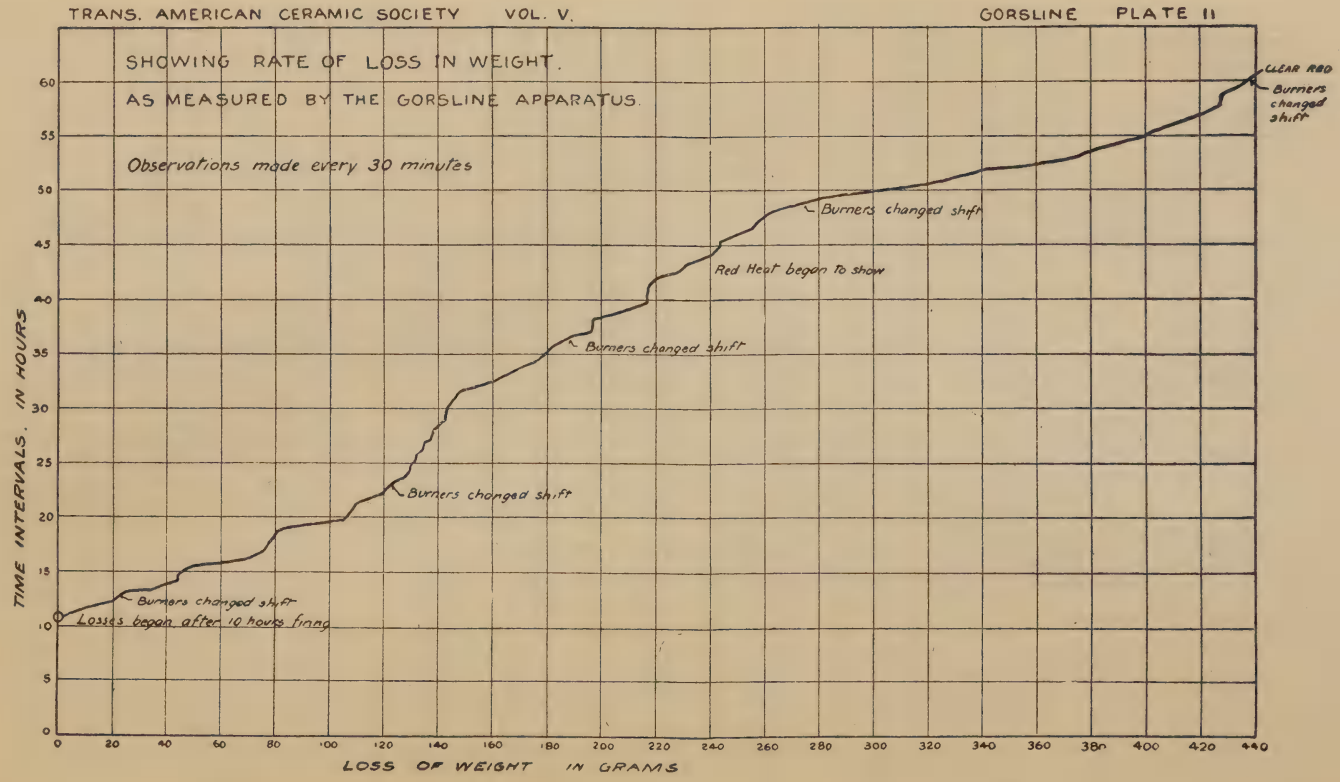
We think this apparatus will help us somewhat in perfecting the conditions in our own factory in regard to this one point.

Discussion by Prof. Edward Orton, Jr.

Mr. Gorsline's apparatus is an exceedingly simple, but exceedingly effective method of showing to burners and others responsible for the burning of claywares, that the loss of water and other volatile substances in clays, is not the simple process that it is popularly supposed to be. It is but a little time since the first printed statements appeared in the clay-trade literature of this country, calling attention to the fact that it requires a red heat to dehydrate a clay, and even now, this statement is met with open incredulity among a large class of so-called practical men. Mr. Gorsline has given them the easiest and simplest manner of proving this point, and while as he says, all the loss may not be water, it at least will convince the most skeptical that *something* is burned out of a clay at red heat, which can not be driven out before.

As a practical tool, for the regular control of burning operations in large plants, I hardly think this process will become important or widely adopted. It is too cumbersome. It would be too much apparatus to move, set up, put in adjustment, and observe, in a plant where from one to five kilns are being started daily. For one kiln at a time, it would be less troublesome.

It would seem that other and easier ways could be reached of getting the same result. For instant it would be just as accurate to put into each kiln, a number of pieces of dry ware, all accurately brought to a standard weight before setting in the klin. If pressed in the same metal die, they would vary but a trifle in any case, and they could be whittled with a knife in a moment, to bring them down so


TRANS. AMERICAN CERAMIC SOCIETY VOL. V.
GORSLINE PLATE II
SHOWING RATE OF LOSS IN WEIGHT.
AS MEASURED BY THE GORSLINE APPARATUS.
Observations made every 30 minutes
TIME INTERVALS. IN HOURS
LOSS OF WEIGHT IN GRAMS
Losses began after 10 hours firing
Burners changed shift
Burners changed shift
Red Heat began to show
Burners changed shift
Burners changed shift
CLEAR RED
Burners changed shift

that they would balance a standard weight on a drug scale or torsion balance.

These pieces, drawn out at intervals of a few hours after redness has been reached, would clearly show whether the clay had reached a uniform weight or not. This method would require nothing but the clay trial pieces, and a small scale or balance. It would not give anything like a progressive curve, from which the rates of loss at different stages could be determined, but it would give the final answer as to when the ware was ready to be carried on up to vitrification.

Regarding the value of the data shown by Mr. Gorsline's curves, I would say that I think that the chief advantage is the education which the man gets who proceeds to do what Mr. Gorsline has done. It pays—tremendously—to prosecute such an investigation. It may help others incidentally, but it is absolutely certain to greatly help the man who plans the work and carries it out. No one can adequately understand or realize these fundamental chemical facts about clay burning, without doing some such work for himself.

When it comes to making exact scientific deductions, or even to making charges of inadequate attention to the firing by the burners, it will require that these curves be most carefully made and studied for a series of burns, before such a course would be safe. For instance, in plate II, where Mr. Gorsline thinks he sees evidence of one of the burners being careless, it seems to me that the evidence is not clear or decisive.

Studying the original curve furnished by Mr. Gorsline, the following losses of weight per shift, and rate in grams per hour are calculated in the following table:

	Shift	Hours	Grams Weight	Rate in Grams per hour
Night Burner	1st	13	22	1.7
Day Burner	2nd	11	100	9.0
Night Burner	3rd	13	66	5.0
Day Burner	4th	11	86	8.0
Night Burner	5th	13	157	12.0

It is not fair to assume that the night burner was less efficient than the day man, because he succeeded in expelling only 1.7 and 5.0 grams per hour for his first two shifts, or that he was more efficient, because he expelled 12.0 grams per hour on his third shift, while the day burner expelled about an equal quantity, 9 and 8 respectively on his first and second shift.

The facts are, that no one could have expelled much water the first shift, without "popping" the pipes. The second shift brought the kiln up to a point when probably the great bulk of the *free moisture* was expelled. By the third shift, the kiln was nearly dry, only a little moisture coming off. This is shown by the fact that the loss was only 5 grams per hour for 13 hours as against 9 grams per hour for 11 hours, on the shift before.

By the begining of the fourth shift, the water again began to come. This time it was the chemical water, which began at the top of the kiln first, and gradually increased as the red heat crept downward. By the begining of the 5th shift, the losses of combined water were becoming general and the rate kept up until the end of the test. Unfortunately, the record could not be carried up to the point where the losses cease, though that point is undoubtly near at hand at clear red heat, and the last observations showed the curve beginning to start upwards rapidly.

If this kiln had been lit at 6 a. m. instead of 6 p. m., it is likely that the work accomplished by the individual burners would have just been reversed. Of course, any wide departure from the proper treatment would show in the curves, and would enable the superintendent to get after the delinquent burner, but conclusions of this sort could only be drawn after a very close study of a number of curves, and with a full understanding of the chemical events taking place in the kiln.

Certainly, the water losses can not become as accurate a guide to the real progress of the burn or the faithfulness and diligence of the burner, as the gain in temperature. In interpreting the water-loss curve, we must make allowances for too many things, while a time-temperature curve, as

plotted from the autographic Chatelier pyrometer is not subject to any such doubt, and may safely be accepted as an evidence of what has actually taken place. However, this instrument is costly, aud available to but few, and hence does relatively little good. There are pyrometers of various other types, which may be used at much less cost.

As the next best thing, to attain an idea of what is going on in a kiln of claywares under fire, I know of no device which is so easily within the reach of everyone, and which will serve to tell so much, as Mr. Gorsline's balance.

MECHANICAL WORK IN THE CERAMIC INDUSTRY.

ADDRESS BY
THE RETIRING PRESIDENT, ERNEST MAYER,
BEAVER FALLS, PA.

A year ago at the Cleveland meeting of this society, you elected me president. At that time, I was unable to be present on account of sickness, and I now take this my first opportunity of thanking you for the honor you conferred upon me.

The American Ceramic Society is now five years old. During this short period its growth and its strength have amazed those who were its founders. Its name is known over this country in circles that we scarcely hoped to reach, and the constant correspondence from abroad, shows that even in those distant points, our work is eagerly sought and its value recognized.

But, this publicity and prominence brings with it obligations which we cannot afford to lightly set aside. We have made a good beginning, and because of that and by means of that, we must keep up our work to the highest possible standard.

I want to make a few suggestions today, in a line where our work seems weak.

The fact impresses me daily that we are sadly behind other industries in our own country. Mind, I don't say other countries, because if we must look to other countries to get aid in the lines I am going to suggest to you, we may rest assured it will never come.

Our society work embraces the whole field of the ceramic industry, and does not, as some people think, refer strictly to the work of the ceramic chemist alone. In meetings held previously, two of my papers have referred strictly to the commercial side of our work, and I want to make a strong plea at this meeting, to see if some enthusi-

asm cannot be raised looking towards bringing the mechanical side of our work into our meetings, to help us out of some of our difficulties.

Outside of a few minor contrivances, there has been practically no evolution in machinery as applied to pottery. Nearly every line of manufacture in our country is now seeking foreign markets, and as we well know, are finding them. We all know that higher wages are paid in the United States than any other nation, yet American manufactured articles are making great inroads into the markets of the world, and the reason is simply the application of machinery and system in our manufacture.

One great difficulty that has always confronted the mechanic, who has brought out new machinery for the more economical manufacture of pottery ware, is this: The requirements of a machine are not clearly understood by him, and when any decided advances are made, it must be done by the really practical potter and the machinist, working hand in hand. Most of the attempts that I have seen made so far, have been where the potter has designed a machine which has failed mechanically, or on the other hand, where a mechanic has designed a machine, and it has not fulfilled the technical requirements of the potter.

I have long been working on several ideas for more economical production of white ware, but so far have yet some important details to be worked out. But in order that my meaning may not be misunderstood, I wish to name a few processes that would make vast differences in the cost of production, if they would be brought under mechanical control.

Most prominently, I would speak of the process known to us as "jollying". I am very positive that every plate, cup, saucer, in fact *everything round*, could be made automatically, where one boy could do more than twice as much as two boys and one man do now. If I am not very much mistaken, such machines will be turning out a very superior class of work to what is now made, inside of two years at the outside.

The process of placing ware in the kilns today, is one of the most expensive methods that could be devised, and

while there is not so much chance here as in the former case for the mechanic, still a very great deal of the heavy, and necessarily expensive work, could be dispensed with.

The process of dipping can be made purely mechanical, and while this statement may sound extravagant in the ears of those who appreciate the value of a good dipper, if any one present is interested enough to take the matter up with me, I will explain exactly what I mean.

Printing is the only process where we see any trace of evolution, and the roller press is here to stay. The identically same machine was used by calico printers in the year 1770; so you see it has taken the potters about 133 years not to invent, but merely to attempt the use of it, and today we can only print in one color. We will only hope it will not take another 133 years to print in more than one color.

The process of making saggers by machinery, is steadily gaining ground in Europe, and wherever they have been used have given great satisfaction.

Brushing all ware in biscuit warehouses ought to be done by machinery, with a proper exhaust fan to take away the dust.

The principal reason that I claim for the introduction of all kinds of machinery in our business, is that on account of the phenomenal increase in the number of potteries in the past few years, and taking into consideration also, all the potteries now building, and just coming into operation, hands must be found to make the ware. Well, we all know the hands will be forthcoming, but how about selling the ware this kind of workman makes? On account of the enormous demand for all classes of earthenware in the past few years, the demand for potters has been far beyond the supply, and the result has been most discouraging to those manufacturers who in the past have prided themselves on the quality of their ware.

The logic of this situation is clear. We need potters, but we need more, the introduction of labor-saving appliances which will place us in position to grow in spite of the shortage of trained help.

Scarcely anything has yet been written by any of our members on the mechanical side. One or two short notes in the earlier volumes is all we have. I hope this little talk will attract the attention of many who have hitherto kept their mechanical papers in the background, thinking that our work was not of this sort. In my opinion, it is particularly needed, both to strengthen the work of the ceramic industry, and to fill out our literature to cover all phases of the ceramic field.

Thanking you once again, for the honor you have conferred upon me, I now invite your attention to the business which the program provides.

ON THE ROLE PLAYED BY IRON IN THE BURNING OF CLAYS.

By Professor Edward Orton, Jr., E. M.
Columbus, O.

The function of a paper before a society like our own, is two-fold. On the one hand, it is to set forth matters of scientific truth, as brought out by investigations in the laboratory or in practice. This is its largest function. On the other hand, it is to stimulate others to study, and to investigate and make known their findings, by placing before them the many fields which remain yet untouched by the representatives of modern science. It is to this end that this paper is directed; no original research has been made to explain its problems, and it is more a query than an affirmation. It simply represents the personal views of the writer gathered by observation in factory and laboratory practice, during the past decade.

The presence of iron in all clays is one of the factors which gives clayworking its fascination, for to this element is due the wonderful capacity for variation which characterize clay products above all others. It is a source of wonder that one element can be capable of producing so vast a variety of effects. The more one studies them, the more marvelous do they become.

When we come to analyze the situation, we soon reach the conclusion that this variety is due to a number of different things, acting in combination. Certainly no single variable could account for the facts. And these influences, so far as known, fall naturally into two classes.

First. Variations in the composition and properties of the clay as regards its iron content.

Second. The treatment of the clay in the burning process.

The natural quality of the clay itself is subject to control or modification to a certain extent, by the clay-worker. The more valuable products, like pottery and encaustic

tiles, justify incurring expense in the preparation of the body, and thus the control of the color, hardness, shrinkage and strength may become very perfect. But for bricks, terra cotta and hollow-wares, the great constructive products, which are used on a tremendous scale, such care in preperation is financially impossible, and we are substantially dependent on what nature has prepared for us.

The treatment of the clay in burning is to a very much larger extent, a matter of choice or skill on the part of the clayworker. He cannot change the character of the clay in most cases, but he can nearly always change the treatment of it in firing, and he can thus often accomplish good results where the clay is itself of poor quality.

VARIATIONS IN COMPOSITION AND PROPERTIES OF CLAYS AS TO IRON CONTENT.

These variations when considered in detail admit of a four-fold sub-division: First, variations in the amount of iron present. Second, variations in the size of grain, or state of distribution in the clay. Third, variations in the mineralogical form in which the iron appears in the clay. Fourth, influence of the minerals accompanying the iron in the clay.

There may perhaps be still other things which go to make up that marvellous and elusive thing which we recognize as the character or individuality of the clay. But, so far as the influence of the iron is concerned, the four headings above undoubtedly account for most of the phenomena with which we come in contact.

Variations in Amount of Iron Present.

Variations in amount are the first recourse to which writers have turned in endeavoring to explain the color phenomena of clay burning. It only takes a superficial acquaintance with the subject, however, to find that this factor is much overrated in importance, compared with the chemical condition of the iron before and after burning, and its physical distribution in the clay.

In general, we may say that no clay is free from iron. The amount may be truly insignificant, as in the purest white kaolins which sometimes only show a few hundredths of a percent, or it may rise to such proportions that the clay ceases to be regarded as such and is valued as an ore of iron. The clay-iron-stone of England and the paint called ochre are cases in point. But the usual proportions are far removed from either of these extremes, and are sufficient to destroy the white color of kaolin on the one hand, and the fine red color of the iron oxide on the other.

Seger has covered this field, as he has most others in the ceramic world, and has shown that clays should be divided into three well marked classes, as regards their iron contents, viz, the white-burning, buff-burning and the red-burning.

White Burning Clays. Without going fully into the conditions which have brought these things about, we may say that the white-burning clays represent those rare conditions, where a rock low in iron has weathered and broken down into a clay, without the intrusion of iron-bearing water or sediments from neighboring rocks. Such a combination of events does sometimes happen, and hence we sometimes find clays which burn white. But since they can only grow by the weathering of igneous rocks, they come almost wholly from the mountain districts, where granites and similar feldspathic rocks occur.

Since transportation of clays in streams is almost certain to result in the blending of iron-bearing sediments with them, it follows that white burning clays in the vast number of cases are primary, viz, found on the site where they have first been formed by weathering. But, in some few instances, as in the Florida kaolins, white clays have actually been transported over long distances and redeposited as secondary beds, without collecting enough iron to throw them out of the white burning class.

The rarity of the conditions producing white-burning clays naturally makes them a very small item compared with the vast bulk of other clays. They probably comprise only a few hundredths of a per cent of the total clay of the

world. Their economic importance is in proportion to their varity, however, and they have thus become a commodity of much value, ranging in price up to $10.00 or $15.00 a ton for the choicest grades.

White burning clays carry from a few hundredths of a per cent of iron to considerably over one per cent. The more ferrugineous contain much more iron than the purer grades of the buff-burning clays, whence it is evident that quantity alone is not a sufficient explanation of the color.

Red burning clays. It has been shown that it is a rare and unusal event when a primary rock breaks down into a clay, or a secondary clay is built up from a floating sediments, without becoming stained with enough iron to bring it out of the white-burning class. In fact, the vast bulk of igneous rocks are ferrugineous, and break down into red burning clays when they weather.

But the remarkable thing in this connection is the regularity of the iron contents of red burning clays. Of the known clay strata, the shales, the glacial clays, and the alluvial clays comprise the enormously preponderating quantity; probably 99 per cent of the whole. And in this great mass, the ferric oxide remains ordinarily between 4 and 7 per cent; occasionally it rises to higher figures. Rarely, under the influence of local causes, it becomes iron ore. But shales from every state in the union, and from every country of the world, the loess of the Mongolian steppes, the glacial clays from Arctic and Antarctic regions, the alluvial clays of Nile, the Ganges and the Amazon, are colored alike with this uniform and ever present constituent.

The explanation seems to rest on the fact that iron composes a small per cent of the known elements of the earth's crust, and that as fast as it is unlocked from its combination in the plutonic rocks which make the shell of the earth, it tends to undergo a concentration in the shale-clay strata. Its fineness and lightness in the form of ferric-hydroxide, which it takes on oxidation, prevents its retention among sands to any large extent. Consequently, sandstones contain less than their share of the total iron. Likewise limestones accumulating from organic sources in

clear water, usually are low in iron. But the shale clays, being composed of the finest sediments, the sludge which travels farthest and settles last, naturally contains the bulk of the ferric hydroxide, which is equally fine and equally difficult to settle.

The origin of the shale-clays, then, is thought to explain their uniformity of color, and the intimacy with which their iron contents have been blended into the other ingredients of the clay. And from the weathering and erosion of the shales, the vast bulk of the glacial and alluvial clays have come, so that we may predict with considerable confidence that red-burning clays, whatever their age or present location, contains between 4 and 7 per cent of ferric oxide.

The red color of red-burning clays is not in proportion to the iron contents however. That is, many clay containing 4 or 5 per cent of ferric oxide burns as fine a red color as others containing 7 or 8. Here again, the distribution seems more important than the amount. While we do not find clays burning red without some considerable iron in their make up, we do not find all clays burning red which contain this amount of iron.

Buff-Burning Clays. This group is less clearly understood than either of the others. In amount of iron content, it varies from 0.50 per cent to 4 or 5 per cent, ordinarily being about 1.5. It overlaps both the preceding groups. White-burning clays burn white because they contains so little iron. Red-burning clays burn red because they contain so much iron. But buff-burning clays do not burn buff because of the exact amount of iron they contain. Often they might burn either red or white, so far as the iron content is concerned. Obviously, quantity alone is a less perfect explanation for this group than for either of the others.

A discussion of their origin leads too far at this present point. Suffice it to say that there are certainly two sorts of buff burning clays, with different histories, and whose color proceeds from different causes. In both, the color is thought to be due to the chemical influence of other elements on the iron oxide.

Variations in the Size of Grain or State of Distribution of the Iron.

The powerful influence of the physical factor is well realized by all who have tried to stain clays artificially to some particular tint. Iron oxide in masses of appreciable size becomes red on calcination at a low temperature, changing gradually to a bluish or violet black as the temperature increases. When added to a clay, it appears as dark colored grains in the matrix of the clay, which is itself changed little or none by this addition. Even when we grind ferric oxide to an impalable powder, and distribute it into a clay most perfectly, it merely causes a darkening or browning of the color, nothing like the buff or red colorations of natural clays.

The failure of these simple synthetic attempts to produce iron colors in clays leads us to a study of the condition of the iron in natural clays. We find two states easily distinguished. First, the precipitated or colloid form, whose fineness exceeds all methods of measurement and which we may fairly assume to be almost molecular. Second, the concretionary or granular form, in which its grains or crystalls are of appreciable size.

The precipitated form is necessary to the development of either a buff or red color. We may easily verify this by precipitating artificially some ferric hydroxide into a fluid slip of clay. It is possible to produce colors as uniform and as free from specks as natural clays, but it is not possible to get some of the tints of natural clays or to get as much color for the amount of iron used as is developed by Nature's methods. As shown in discussing the origin of the shale clays, the iron has been associated with the clay minerals from the very time of formation. The primary clay was usually deeply stained by the solution of iron which formed with it. The soft gelatinous hydroxide has enveloped its grains form their very origin, and left each tiny particle covered by its coloring film. Every succeeding process tends to increase this uniformity, grinding, transportation, erosion, deposition in swamps, all tend to increase the iron and to reduce its blend to perfection.

Thus in the ordinary red-burning shale-clay, for instance, it becomes impossible to distinguish the hydroxide, from the clay minerals. The sand, and the mica, and the concretionary minerals of all sorts, can readily be separated by screens or by sedimentation processes, but the pulp which remains inseparable to the end, contains the bulk of the iron, and is red-burning, while the coarser matters which have been separated out, may burn light or dark or speckled, but hardly red. In fact the question has been raised as to whether iron is not chemically combined as a part of the clay substance. No proof of this view has ever been attempted, and all the evidence obtainable points the other way. For instance, dilute hydrochloric acid will take out nearly all the iron from a red burning clay, leaving a residue in which the clay substance has not been sensibly attacked and which burns light colored or white. If the iron were a part of the kaolinite, its withdrawal would leave the molecule decomposed, and the alumina also would then dissolve, as its bond with silica would be broken. But such is not the case. Hence, while we can readily see how such a view might be suggested by the extreme intimacy of the mixture, and the uniformity of the color produced by it, still it cannot be defended as a scientific fact.

But here, again, we reach a point where qualification becomes necessary. The occurrence of the iron in infinitely finely divided form is necessary to the development of either the buff or the red color. But, the presence of iron in this form, even in connection with the quantity, does not in itself necessarily cause the red or the buff color. The addition if even a little red clay slip to a buff slip will produce a body which burns salmon or flesh color or terra cotta, while other buff bodies may easily be found containing twice as much iron as the experimental mixture contains. Thus it appears that each clay is buff or red as the case may be, from some cause other than the amount or fineness of distribution of the iron.

The concretionary forms of iron in clays include all particles which were not in the jelly-like or colloid state when they entered the clay or which have been drawn to-

gether into masses by the obscure forces which we call crystallization or concretionary growth. It does not matter what the force has been which collects iron into granules or what the history of the granules of iron in a clay has been. The mere fact that it *is* in granules, is sufficient to determine its effect.

In general, we may say that its coloring power is almost nil. That is, its power to color the matrix or real pulp of the clay. It will produce colors in the broad sense, for we add iron to buff-bricks to make them into grays or speckles. But the change in color is due to alternations of black and buff, and not to a blending of colors, or, the formation of a new color. This segregation of the iron of a clay into granules, is the cause of much trouble to the clayworker. With this trouble comes some benefit. The trouble consists in speckled, spotted, pimpled, rough and unsightly ware. The benefit comes from making a virtue of necessity and creating a market for such speckled and mottled color as concretionary iron will produce. The face-brick industry has shown a wonderful example of this in the last 20 years, and now millions of mottled and speckled and gray bricks are produced with good artistic results. Yet, the real reason for their appearance was the inability of the clayworker to always avoid such manifestations in his wares.

We find that even concretionary grains of large size do contribute some little to the color of the body-matrix of a clay, when the firing temperature becomes sufficient. The iron assumes a silicate combination, and permeates the surrounding matrix, forming a ring or shell of yellow or red or black color, whose size depends on the fluidity of the iron silicate and the duration of high temperature. But, practically speaking, concretionary iron is not responible for the colors of clay.

The Mineral Forms in which Iron occurs in Clays.

The ferrugineous minerals which are most commonly found in clays are:

(a) Ferric Oxide, anhydrous, or in various stages of hydration.

(b) Ferrous Carbonate.

(c) Ferric Sulphide or Pyrites.

(d) Ferrous Silicate minerals, like Biotite, Hornblened and many others.

(e) Ferric sand minerals, like Magnetite, Menaccanite, Chromite, etc.

The two latter divisions do not contribute any large quantity of iron to ordinary clays, probably not over one per cent. and generally much less than that. They are represented by small amounts in all clays, but they affect the clay chiefly by forming minute black slag spots or black specks in the ware, according as the heat has fused them, or left them unslagged. It is from the three first minerals, therefore, that we derive the principal beneficial or detrimental effects of iron.

These three minerals are sometimes all found in the same clay, and it cannot be said that any one is confined to any particular kind of clay. Still, some sort of classification by location is possible.

In the following discussion, consideration will only be given to the secondary clays, which compose the bulk of our clay wealth. The primary clays, although they include nearly all of the white-burning kaolins and china clays, form such a minute part of the vast masses of clays in general, that they need not be considered in this discussion, and the red burning primary clays are of small economic importance.

Among the secondary clays those of recent geological age, like the alluvial clays which cover the present river valleys and bottoms, almost invariably contain their iron in the form of ferric oxide or hydroxide. Ferric sulphide and ferrous carbonate are not unknown in such clays, but they are quite unusual.

In the next group belong the glacial clays, which were deposited like a blanket over the northern half of this continent, by the great ice cap or continental glacier which invaded us from the north in recent geological times.

The rough hilly country was covered with the ice sheet, the tops of the elevations ground off, the valleys filled in

with the debris, and over all, as the ice retreated to the north again, the great sheet of clay was left behind to form the soil. In view of their origin, we cannot expect glacial clay to be uniform in any respect, either in size of the mineral particles, or the kind of minerals represented, or their chemical condition. And the facts justify this view, for no sedimentary beds vary so widely in character as those laid down by the ice.

In the glacial clays, ferric hydroxide predominates; especially is this true on the surface. But, where deep cuts are made into glacial clays, we not infrequently find them taking the form of blue, tough, adhesive hard-pan, in which the iron is ferrous carbonate. It may be fairly said that time has elapsed since the glacial period, to convert the iron salts of the deeper strata into ferrous forms. But, in many cases, the other conditions did not favor the change. Hence, while ferrous beds are common, at times almost reaching the surface, they are more often found deep under cover.

Clays of ancient origin, such as the fire clays and shales, contain their iron most commonly as the ferrous carbonate or the sulphide. The reason for this is clear. Nearly all such strata contain, or have contained, more or less carbonaceous and sulphurous matter, and during the enormous periods of time since their deposition, have been subjected to bacterial action, heat, and pressure. The reduction of the iron, and its combination with the CO_2 and S thus produced is a natural event under the circumstances.

All fossil clays are not necessarily ferrous, however. We have among the Carboniferous and also in the Permian, many conspicuous examples to the contrary. Red shales and red clays, which contain their iron largely or wholly in the ferric condition, are not uncommon, geologically speaking.

The sulphide of iron is a "free lance," so to speak. It is common, both in old and young rocks. It is easily formed and as easily decomposed again. Oxydation, even at common temperatures, rapidly converts it into the sulphate, while similarly, the sulphate is easily reduced by decaying

organic matter to the sulphide once more. Hence, its presence means either recent reduction, or that no opportunity for oxydation has recently occurred. It is called a ferric mineral, but in the conditions of its formation, it accompanies the ferrous group, and when it decomposes it invariably yields the ferrous oxide first. So, while it is a ferric salt, it ranks with the carbonate in its tendencies in the clay.

But while shales and fire clays characteristically contain their iron in carbonate or sulphide form, it is also true that the exterior of most shale-clay and fire-clay beds have been more or less deeply oxydized by weathering processes. Whatever is easily accessible to air, percolating waters, and the mechanical action of heat and frost, is likely to become ferric, while rocks below drainage level, or covered deeply by other strata, are apt to remain ferrous.

The effect of these various minerals on the color of the clays is not in itself strongly marked or characteristic. That is, as good a red color may be developed from a clay containing its iron as ferrous carbonate as from ferric hydroxide. But the mineral form is of importance nevertheless from two causes. First, the tendency which some minerals show to crystallize or gather in concretionary masses. Second, the great differences in treatment which the different minerals require in burning.

As to the first tendency, it may be said that all forms of iron crystallize or gather in concretions. It is simply a question of degree. Ferric oxide and hydroxide is least prone to do so. In fact, where ferric concretions are found in clays, they generally represent reoxydized concretions of the carbonate, rather than accumulations originally ferric. Consequently a clay containing ferric oxide exclusively is apt to be of an even color on burning.

Ferrous Carbonate, on the other hand, seems to exist in disseminated form or in concretions with equal ease. In fact, both forms generally exist side by side. A red burning matrix will be full of black specks, produced by the lumps of the same mineral which produces the red color. Thus in dealing with a clay in which ferrous carbonate is known, there is every reason to expect that finer grinding

and greater care in preparation will be necessary, unless the ware is one in which the presence of specks is not prejudicial.

Ferric Sulphide, on the other hand, is invariably found in granular form. These granules may be large or small, but they are never small enough to give a red color. They invariably show up in the burned products as black specks or slagged spots, and hence in most wares are an unqualified nuisance. An interesting case of some kaolinitic clays from the Phillipines recently showed pyrites in every sized grain from 8 mesh down to 200 mesh, the latter requiring a glass to see the grains clearly. The pulp passing the 200 mesh seive burned gray, evidently from the little grains of pyrites which the seive had not been able to retain, as the clay itself burned pure white, in occasional places where no sulphide of iron was present.

The effect which these three minerals exert on the color of the clay through differences in burning, will not be discussed at this time except to say that ferric hydroxide is the easiest to burn successfully, the carbonate next and the sulphide most difficult.

The Effect of Other Minerals on the Iron Color.

The considerations involved in the quantity, the distribution and the mineral form of the iron, have been shown to be accountable for much of the variety of color in the common or secondary clays. But, it has been shown that some of the fundamental phenomena are still unsatisfied by these causes. The development of the buff or yellow color is the chief of these. We have seen that we cannot produce it synthetically with anything like the ease with which the red is produced. In fact, the writer has never succeeded in making a good buff from a white, by addition of iron. The use of iron in white clays has given a pink series, but no yellow. It seems that the latter is due to another factor, viz, the masking or suppression of the iron color by other elements in the clay.

Seger has classified buff burning clays into two groups. First, those high in iron, which would burn red normally,

but which contain so much lime as to destroy the red iron compound and form a yellow lime-iron compound in its place. Second, those clays low in iron, which would burn to a pale red at best, but which contain enough alumina to form an alumina-iron compound of a yellow color. Seger thinks the destruction of the iron-red color in these two cases is accomplished by similar means, and that lime differs from alumina in being the stronger and more active base, and thus being able to overcome the greater quantity of iron.

All agree on the former proposition. The effect of lime on the iron-red color in clays is undeniable. The reaction is in daily use as a means of controlling iron colors, all over the world. But to this second proposition, the writer can not give unconditional assent. The evidence Seger marshalls is strong and undoubtedly points to his conclusion. But if it were true, then synthetic mixtures should easily give the buff color, which has not been the writers experience. We certainly find an amazing uniformity in the color of buff-burning clays, while their iron-alumina ratios fluctuate very greatly. Some fire clays contain 40 per cent. of alumina and 0.5 per cent. of iron, and burn a good buff. Others contain 15 or 20 per cent. of alumina and 2.5 to 4 per cent. of iron and burn to almost exactly the same tint. Other clays of different geological history, containing about the same alumina and iron, burn a fine red color.

It seems as if some other influence than either the amount of iron, its distribution, or its masking by other oxides must be brought in to explain the buff-burning fire-clays. The significant fact is that fire-clays occur so very generally in connection with coal veins or other accumulations of organic matter. Wherever carbon has been accumulated in bygone ages, there we find buff-burning clays immediately underneath. Often the coal has been washed away while still soft, and disseminated, but the fact that it had been, is proven by the fire-clay vein which is left behind. In fact, the fire-clay more uniformly marks the coal swamp, than the coal itself.

This connection, so constantly shown all over the world, in strata of all ages where coal has grown, certainly seems

significant. Whether the swamp growth has formed certain organic salts of iron which influence the color, or whether it is by the removal of other substances than iron, or whether it is by stimulating the growth of concretionary forms of iron and thus preventing the distribution of the color, can not be stated.

On the other hand, in support of Segers theory that alumina masks the iron and produces the buff color, the fire-clay beds of New Jersey, the flint clays of Missouri, and many of the Cretaceous fire-clays of Germany, may be cited. They do not occur in connection with coal veins, nor is it reasonable to suppose that they are composed by the erosion of other carboniferous fire-clay beds, and deposited without sensible blending or intermixture with red burning sediments. In fact, their occurrence, alternating with beds of sand, gravel and red-clays, gives the lie to any such assumption.

The most we can say at present on the cause of the buff color of the fire-clay groups, is that they generally contain less iron than is needed to produce a red color; that this iron is distributed in the most perfect manner possible. Segers alumina theory does not seem to wholly fit the case, and the geological history of fire-clays and their production by swamp growth and carbon accumulation is after all not a cause. There must be a difference in compound, or amount, or distribution, or their geological history could hardly avail to produce a difference. The settlement of this most interesting point is one which invites the attention of the ceramic investigator.

The effect of the accompanying minerals on the color generated by iron is not confined, however, to the reaction known as "masking," which have just been discussed. There is another class which is a prolific cause of trouble in getting the usual iron colors, but whichhas no off-setting advantages in the way of producing desirable new colors. I refer to the presence of reducing agents, like carbon, hydrocarbons or organic matter, or sulphur compounds. These substances all burn out from a clay readily under favorable conditions. They do not, of themselves, add to or subtract

from the colors wrought by iron. But, by virtue of their superior affinity for oxygen, they prevent or delay the iron from playing its customary role, and hence cause untold trouble in the burning.

The ancient or fossil clays are the ones most affected by these troubles. Recent clays, like the river and glacial beds usually contain some trifling amount of organic material, but it is still woody in nature and hence easily combustible. It burns out early in the process of firing, and leaves the ware spongy and easily accessible to the kiln gases. Hence, it does no harm except when it becomes excessive in amount and thus makes too much heat.

But shales and fire clays have been generally altered by heat, pressure and bacterial action, and their organic matter has been turned into graphite, or coaly matter, or bituminous or asphaltic cements which penetrate the clays most intimately. Also sulphur, which is seldom found in quantity in the surface clays or the young clays, is nearly always common in the old or fossil clays.

The most difficult clays to burn which the clay worker ever meets are the bituminous and pyritiferous shales and fire clays. It is safe to say that the losses incurred in clay burning center largely around the troubles which these minerals aggravate, if not actually cause.

THE TREATMENT OF CLAYS IN BURNING.

We have now seen that the occurrence of iron in clays is so varied as in itself to suggest a cause for the complexity of results which practice demonstrates. And, there is no question that much of the richness and variety in clay products does come from just this fact. But, the treatment which the clays receive in burning is a matter of fully equal concern to the clayworker, because the strength, durability, beauty and color, texture, in fact the whole quality of his product, is affected or controlled thereby. It is a matter of of even greater concern, because it is largely under the control of the clayworker himself, and is thus a direct key to commercial success, while he cannot exercise a similar con-

trol over the composition of the clay itself, except for fine wares, out side of the range of this discussion.

It is strange perhaps that iron should play a part of such exceeding prominence in clay burning, but such is the case. It not only has the power to color the products though a multitude of varying shades and tints, some beautiful, others unsightly, but it also has the power to cause the ware to swell up, to become deformed, to become pimply and rough on the surface, to become spongy and weak, in fact perfectly worthless. In order to guard against these troubles, it is necessary to understand their causes, and this involves an understanding of the whole theory of the burning and vitrification of claywares.

Clay burning is chemically a most complex process; it consists of a series of reactions overlapping one on the other in such a manner that one can never trace the exact beginning or end of any single one. In general, we may divide it up into three principal kinds of reactions, and these divide the burning process roughly into three corresponding stages.

First. The dissociation of materials which are unstable at high temperatures, and the expulsion of the volatile portions from the mass of the clay.

Second. The transformation of the non-volatile elements from less stable into more stable forms by absorption of gases from without the mass.

Third. The amalgamation at an elevated temperature of the various residual inorganic substances left by the two preceding reactions, into a more or less perfect silicate compound.

Of the reactions which make up these three classes, there are some which are necessary to the successful execution of the burn; others whose influence is seemingly not necessary or important; others which cannot be construed other than injurious to the product, and to be avoided as far as the case permits.

The division of the burning into these three periods is of course arbitrary, since the reactions overlap, and at no

time can it be said that one process only is going on. However, it affords some measure of convenience and intelligibility to a process which is otherwise complicated, and may be justified on that account.

THE DEHYDRATION PERIOD.

The reactions of this period are only the preliminaries by which the minerals of the clay are brought into condition for the final combinations which culminate in the finished ware.

The reactions are chiefly

(a) Expulsion of hygroscopic water from the clay.

(b) Combustion of carbonaceous matter.

(c) Distillation of S from pyrites, leaving FeS.

(d) Dehydration of Kaolinite, Ferric hydroxide and other hydrous minerals.

(e) Decarbonization of carbonate minerals.

Taking each in turn we may describe them as follows:-

Expulsion of Hygroscopic Water.

This is not a chemical process, but its power to interrupt or defeat chemical processes is so great that it seems proper to give it a place.

Water is vaporized at 100° C., and theoretically cannot exist longer in the clay in the free condition after that temperature is reached. But practically, the pores of the clay-ware retain it obstinately until temperatures considerably in excess of 100 degrees are reached in the general atmosphere of the kiln. The kiln is hardly to be considered dry until the atmosphere of its coldest part has reached 150° C.

The power for ill which this process exerts lies in the delaying of other processes, by which the time devoted to their execution is shortened. No oxydation or dehydration can occur while the mechanical water is present, and further, no senible headway can be made in heating the ware up until the water is gone. And since the heat required to evaporate water is 537 units, and since the specific heat of water below boiling is five times as great as that of clay, and since the specific heat of steam is twice as great as that

of air, it is plainly to be seen that where two pieces of ware, one wet and one dry, are both subjected to the same kiln gases, that the dry one will attain a high temperature rapidly, while the other will gain no heat for a long time. Hence, when the temperature reaches the point where some other chemical reaction is due to begin, one piece is prepared and the other is not prepared for it.

The practical importance of this point is exceedingly great. The simple remedy is to never set ware in the kiln unless it is dry, or if for any reason ware must be set which the burner knows is too wet, or if some wet ware has been interspersed through the dry ware, then he must convert his kiln into a dryer, and fire it so slowly and so long before venturing to raise fires, that all original inequalities of water will be removed.

Many very intelligent burners and managers believe that the swelling or bloating of clay wares is due to the water escaping at high temperatures. In fact, the writer himself advocated this theory in 1892. But further study has shown that wet ware is only the indirect cause of the trouble. The actual swelling takes place by another chemical reaction. But if the water had been properly expelled first, the second reaction would not have happened.

The picture (Fig. 1) shows an example of this difficulty which is common in most paving brick plants. Two brick, stuck fast to each other in burning, one swelled, and the other square and true. The swelled brick was set damp, while the square one was dry. Yet both must have had the same conditions of time, temperature and chemical composition of kiln gases.

Combustion of Carbonaceous Matter.

This reaction is one which may cover a very great heat range depending on the kind of carbonaceous matter pres: ent. There are several principal forms:

1st. Vegetable tissues, fresh or but little altered, such as rootlets, grasses, leaves, bits of wood, or wood pulp, turf, or peat-like manner.

2nd. Vegetable or animal matter, greatly altered by

FIG. 1. SEE PAGE 394.

FIG. 2. SEE PAGE 396.

partial decay, or partial distillation under heat and pressure. Here belong the lignitic matters found often in ball clays, and the bituminous and asphaltic matters found in the shales of the Carboniferous and earlier periods.

3rd. Inorganic carbon minerals, in which any organic structure they may have had has been blotted out by the distillation and heat treatment they have undergone. In this class belong the graphite found in the shales and slates of the Appalachian mountain district.

Besides these substances which naturally occur, there are others, added for various technical ends, which fall more or less directly into these classes: for instance sawdust, tan-bark, and straw in the first, and anthracite coal-dust and coke-dust in the third division.

The first class, or woody tissues, burn out rapidly and at low temperatures. Wood catches fire even as low as 250 or 300 degrees, and if the amount is small, this class of substance rarely does any harm. If it is large, as in the making of fire proofing or terra cotta lumber, where some times as much as 40 per cent of sawdust is used, it is capable of ruining the ware, by bringing the heat up too fast.

The second class, or bituminous matter, is the most common and most dangerous form in which combustible matter may be found in clays. Its danger lies in the fact that it is a partly volatile substance, solid at ordinary temperatures but which readily breaks up into a rich combustible gas, and a residue of carbon or coke, by the raising of the temperature. Three to six percent of such carbon is often found in a shale clay, and this means, in a kiln of 50000 bricks, six to twelve tons of fuel, or a third enough to burn the kiln, if its heat could only be utilized.

The volatile portion of these bituminous matters naturally burns very rapidly and with intense heat, when the temperature reaches the point where it is expelled. In fact its combustion raises the temperature of the kiln so rapidly when it once catches fire, that it urges on the completion of the distillation far faster than the normal heat of the kiln would do, and does not cease until every bit of volatile matter has been expelled and combusted. But by this time,

the temperature of the kiln will likely have passed all safe limits and the ware have become swelled, melted and stuck fast together.

Fig. 2, represents a collection of bricks from Lorain, O., where a black shale containing 6 per cent. of bituminous matter was being worked. Spalls of this shale thrown into a hot kiln would blaze nicely for several minutes. The company was making brick by the dry process. After spoiling many kilns, they were finally told to shut off the air supply, when the gases took fire, and let the conflagration within go on slowly until it finally burnt itself out. The leakage of air through the walls of the kiln and through the daubing of the fire holes and wickets was sufficient to combust more gas than was advantageous. Unrestricted air supply simply melted the bricks. Five days of this slow distillation was sufficient to drive out all but the solid coke residue. The kiln was then opened, air admitted, the last of the carbon burnt out and the work proceeded.

The brick on the top shows the brick properly burnt. Those below show the results of unrestricted air admission and consequent melting. The danger from this form of carbon is not wholly confined to the too rapid combustion of the gases. The residue of the carbon left in the clay when the gas goes out, is still a troublesome problem. It is so fine, so evenly distributed, and so intimately blended with the clay, that it is much more difficult to burn out than ordinary graphite or coke or anthracite slack.

The cut (fig. 3) shows a collection of draw-trials made from a moderately bituminous shale from Cannelton, Indiana. The shale had passed a 16 mesh screen and was worked by the plastic process. Beginning on the left, the first trial was drawn after 20 hours firing, 10 of which were above red heat. No. 2 was drawn at 24 hours. The color of the uncombusted carbon in the core was paler, but not reduced in area. No. 3 was drawn after 30 hours. The carbon had burned out somewhat, as was shown by the reduced size of the black spot. No. 4 was drawn at 37 hours, showing the carbon practically gone. The kiln was then fired till 44 hours, and No. 5 was drawn when cold. The

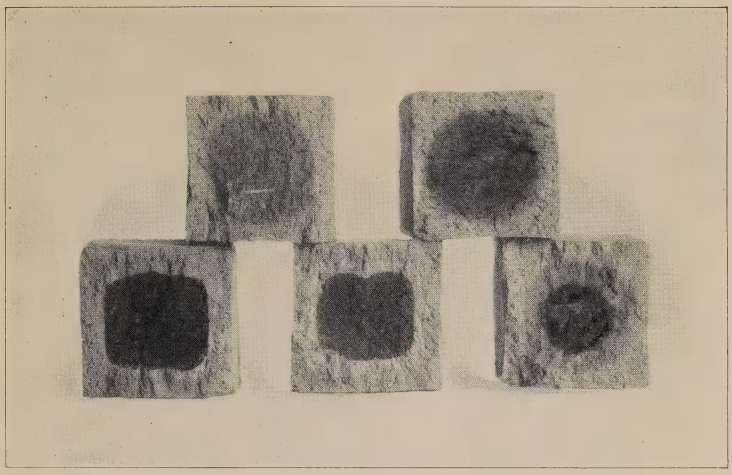


FIG. 3. SEE PAGE 396.

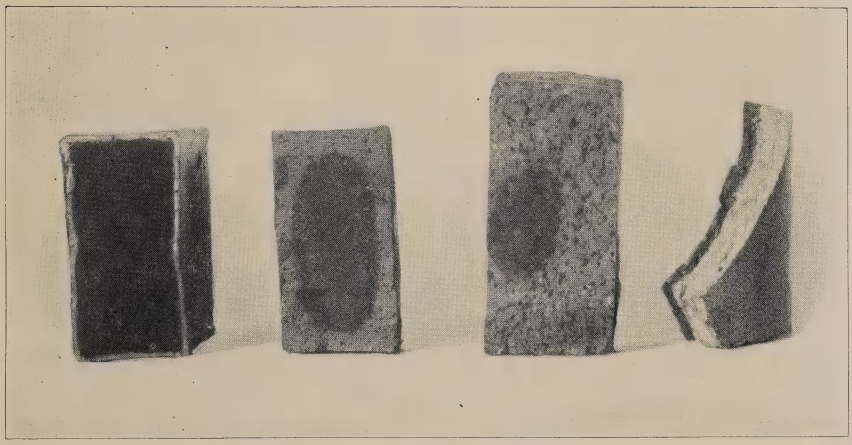


FIG. 4. SEE PAGE 410.

central core is of a brighter, more orange-red color than the exterior. This shows first in No. 3, encircling the small black core. No. 4 shows it also, but No. 5 shows it most strongly developed. This difference in color is due to the fact that the iron oxide has been reduced by the carbon, and although reoxidized perfectly, it never takes the same color again. It is, in fact, the same reaction discussed by Bleininger under Notes on Flashing*

Considering the small size of these brickettes, and the special regulation of the test kiln atmosphere for oxidizing the carbon, the above series is a very instructive example of the slowness aud difficulty with which this is accomplished. Where a whole kiln of such wares is to be treated at once, the difficulty and necessity for time are correspondingly increased.

The third class, or non volatile carbon, is not often a source of danger or inconvenience to the ware, especially in relatively coarse or granular forms. It burns only by slow oxidation, or glowing, and without flame. It does not burn out until a good red heat is reached, and requires that time be given for this to take place. Otherwise, it is seldom a cause of trouble. In fact, it is often purposely added to a clay, to make a better distribution of heat in the kiln. The brickmakers of the Hudson River district are especially addicted to the custom.

As will be seen later on, the carbon compounds are not *in themselves* particularly troublesome or hurtful to a clay, for they always disappear in the burning if given any chance, and are not often in sufficiently large quantity to exercise any great effect on the working qualities of the clay while raw. But they are a most fruitful cause of trouble indirectly, by their influence on the iron compounds, as will be shown later.

Distillation of Ferric Sulphide. FeS_2 is a mineral which is perhaps responsible for as much of the trouble incident to clay burning as any other single one. Its heat reaction is peculiar in the fact that the sulphur is not driven out at one

*Transactions Am. Ceramic Society, Vol. II page 74.

time, but in two stages. The first decomposition is represented by the formula

$$FeS_2 + \text{heat} = FeS + S.$$

This reaction can easily be verified by heating a little pyrites in a glass tube, to the point of redness or just below. The first molecule of sulphur comes off, forming yellow oily drops on the side of the glass; the black residue remaining is found to contain one-half of the original sulphur.

The second molecule of sulphur is obstinately retained by the iron, and can only be removed by roasting with free oxygen in abundance. The point at which this is completed will depend on the porosity of the clay, the rapidity with which the heat advances, and the purity of the hot air which has access to the clay. If it is largely diluted with combustion gases, the oxidizing power is, of course, much cut down.

It is safe to say that in ordinary cases, the first molecule of sulphur from FeS_2 is expelled and burns to SO_2 or SO_3 at temperatures of 400 to 600°C. It is equally safe to say that that the last molecule is not expelled at all, unless due opportunity is given. Under favorable circumstances, it undoubtedly is roasted out by 900°C, and perhaps earlier. Where this does not occur, the FeS fuses, forming a black slag.

Dehydration of the Hydrous Minerals. The chief of these is the kaolinite, which loses its water at a low red heat, variously estimated at 550° to 650°C. It is now the opinion of the writer that the expulsion of combined water from clay, or from any other hydrous mineral, cannot be the cause, in itself, of any of the troubles incident to clay burning. An opposite view was entertained and published in 1892*, in which the swelling and blackening of red and buff burning clays was ascribed to this cause. Langenbeck in a private communication, was the first to call attention to the impossibility of this explanation being true. There is no doubt that clays have, at the completion of the dehydration reaction, a structure more porous than at any time, before or

*Ohio Geological Survey Report. Vol. VII, page 81.

after, and the swelling of clays is now explained in another way.

Besides kaolinite, water of combination is found in various other minerals, gypsum, talc, various zeolites, and the hydroxide of iron. and manganese. Undoubtedly they all lose their water quietly and easily, as kaolinite does, and at as low a temperature.

The Decarbonization of the Carbonates. Of these minerals there are four commonly found in clays, and several may be found together in one clay. These are: Carbonate of calcium, carbonate of iron, carbonate of magnesia and dolomite.

The carbonate of lime, so common both in and out of the clay strata, is a constant factor in clayworking operations. Only two classes of clay are presumptively free from it, viz., fire-clay of the coal measures and alluvial clays of recent origin. Shales may or may not be free, and bog clays and glacial clays are pretty sure to contain it.

The heat reactions of calcium carbonate have been carefully studied by the lime and cement chemists, and from them we know more of its behavior than from the researches of clayworkers. It decarbonizes at 600 to 900°C, the time depending on the composition of the kiln gases. The more steam is present, the more readily is the gas given off, though why that is so, is a matter of conjecture. The decarbonization is certainly delayed if CO_2 is present in large quantity in the gases, and CaO once formed will actually revert to $CaCO_3$, if the CO_2 gets too high a constituent in the surrounding gases, and the temperature is not too high. Above 900°C, the reabsorption of CO_2 is not possible, until the temperature drops again.

Carbonate of iron, or siderite ($FeCO_3$) is a very abundant mineral in clays. As already indicated, it is found chiefly in the shale, and generally not in clays of recent deposition. The former greatly outweigh the latter in quantity, but the latter are more widely distributed and accessible as well as more plastic, and hence respond more readily to the clayworkers needs. It is natural, therefore, that

the clayworkers should have avoided the former as they have done.

But in comparatively recent times, shale clays have sprung into great favor, chiefly for their undoubted fitness for making vitrified wares, like sewer pipe, paving brick and hard building brick. And in using them, clayworkers have come into frequent contact with a series of phenomena for which their older practice with superficial clays had not prepared them.

The behavior of $FeCO_3$ on heating has been made the subject of one incomplete series of tests in my laboratory. We found that at 425°C, the CO_2 had been fully expelled. How much lower than this point the reaction began, we have not yet determined, as the first brickettes drawn at 425 showed the CO_2 already expelled. The test was made on a kidney iron ore which contained about 35 per cent. of iron as carbonate and 6 or 8 per cent. as ferric oxide. The ground ore was plastic enough to endure being molded into brickettes without the use of any clay as a binding agent.

These results were a surprise, as the idea had been accepted previously that $FeCO_3$ retained its CO_2 vigorously till 800 or 900 degrees.

The decomposition of magnesium carbonate and of dolomite takes place at about 400°C and 600°C. The latter figure is not accurately known, but it is known to be between the point where calcite and magnesite break down, and much closer to calcite than to magnesite.

The small quantities and infrequent occurrence of magnesite in common clays makes these figures of much less moment to us than is the case with the carbonates of lime or iron.

The decomposition of the carbonate minerals is a very important and significant thing in a study of the vitrification process in clays, on account of the reactions which begin between the basic oxides thus formed and the silicates of the clay. But their interest in this present connection is chiefly because of the carbonic acid gas which must be expelled before the oxydation of the iron can enjoy a free scope. The genuine obstacle which the carbonate clays

offer to satisfactory oxidation, is apparent to all who deal with them. Limey clays especially resist it, because their pore system is clogged with the escaping CO_2 until solate; 900° or thereabouts.

The heat behavior of ferrous carbonate differs from that of $CaCO_3$ or $MgCO_3$, in the fact that FeO, which remains when the CO_2 is set free, is not a stable compound. In fact, it is one of the most unstable; it is difficult for the chemist to produce and keep FeO, free from oxidation. Consequently, the breaking down of the $FeCO_3$ is only the signal for a second reaction, viz., the oxidation of the resultant ferrous oxide to the more stable ferric form. This reaction will be fully discussed in the succeeding section.

In the foregoing, has been set forth in some detail the general behavior of the minerals during the heating from atmospheric temperatures up to 700°C. No single clay is likely to contain all of the various minerals here noted. But on the passage of any single clay to this temperature, it is believed that the order of the changes and their results would be about as described.

The Physical Structure of Dehydrated Clay. It is important for us to realize the physical condition of a clay after this stage has been reached. This can easily be observed by any one by drawing a piece of clay ware from the kiln, when it has attained bare redness in daylight, and cooling it promptly.

The porosity is greater than at any other stage. The mass retains the structure given it during manufacture. That is, the pores occupied by the water while the ware was plastic, still remain. To this porosity is added that produced by the loss of combined water from the clay substance, the loss of CO_2 from some of the carbonates, the burning out of the organic matter, and the partial distillation of the FeS_2. The shrinkage has not begun. The clay measures just as it did when dry. The hardness is very low—scarcely greater than that of thoroughly dried clay. Also, the strength is very low—not being much increased by the burning process so far.

The color will ordinarily have changed from the natural clay color, to a very pale yellowish-red or salmon, in those clays which contain much iron. In fact, in fire-clays which ultimately burn buff, the color at this stage is apt to be pinkish-red, which fades and yellows as the heat rises. The same is true of calcareous clays, in which the iron color is masked by the lime. These clays are red early in the burn, becoming yellow only after the lime becomes fully caustic.

The Oxidation Period.

As set forth earlier in this paper, the fundamental work of this period is the transformation of the more volatile elements of the clay from less stable to more stable forms by the absorption of gases from without the mass. This simply means that FeO or FeS must be converted into Fe_2O_3, before it is safe to proceed with the next step in the process.

The advisability of giving a separate subdivision of the whole process of clay burning to this small portion of it, may seem to some to be doubtful. Especially, when it is reflected that this stage is most important in red burning clays, less so in buff ones, and not even noticeable in white burning bodies.

But, it has been the experience of the writer, that the difficulties and losses in the burning of crude claywares are more largely referable to mismanagement of this phase of the burning than to any other; perhaps more than to all the other causes combined. And, while there is no actual line of demarkation between the dehydration, decarbonization, and oxidation reactions, all of them overlapping more or less, still it seems essential to create in the mind of the clay burner the feeling that separate and clearly marked stages exist, and that he must satisfy himself of the completion of each, before passing to the next. Lastly, while oxidation may take place at any point on the lower end of the temperature scale, it cannot take place at all if the limits of this period are once passed. Thousands of dollars would be saved annually, if clayburners could be brought to see that in passing above this temperature line, they are taking an

irrevocable step, and that clay not well oxidized at that time is practically sure to be spoiled.

It has already been hinted that the oxidation of FeO to Fe_2O_3 is not only an easy chemical reaction to perform, but even a difficult one to prevent. But also, it has heen hinted that it does not take place with facility in the burning of clays. It seems apparent, therefore, that when such an affinity as FeO and O exhibit is unsatisfied after hours of exposure to red heat in a kiln, surrounded by a constant flood of gases in which free oxygen exists, that there must be some very definite and clear-out influences which are operating against this reaction. Such is the case. There are five reasons which deserve mention in this connection.

Mechanical Action of the Clay itself. When we calcine ordinary copperas at a low red heat, we produce Venetian red, the brightest and most beautiful red which iron oxide is capable of forming. Moreover, the reaction is easy, quick and complete. But when we set free 5 or 6 per cent of FeO in a clay, we must recollect that it is distributed throughout a mass of fine particles closely packed together, which form a very effectual mechanical bar to contact of outside air.

Furthermore, we must reflect that the air can only circulate through the mass of the clay through the infinitely fine capillary system established by the water of plasticity or the almost equally fine interstitial spaces left between the grains of a dry-pressed body. We have seen that the body becomes somewhat more porous after the dehydration changes are complete, but the total amount of such porosity is, after all, not great; usually 25 to 35 per cent of the mass of the clay Into this structure, (spongy structure I had almost said, but spongy gives a wrong idea of the openness) the fire gases must penetrate to accomplish oxidation. And while they will do so in time, is it a cause for wonder that time is required? Remember, that the gas is not forced in, or sucked out, by any physical differences in pressure.

The piece of clay is merely lying in an atmosphere of flowing gases, and from this it must gradually absorb the oxygen which its interior particles crave, and must carry it

through the labyrinth of pore-spaces to the little particles of the ferric oxide waiting to receive it.

Hindrance Caused by the Evolution of Other Gases. As already pointed out, the $FeCO_3$ breaks up early, and its CO_2 should have been completely expelled from the clay considerably before dehydration sets in. But, it may happen that the temperature proceeds upward faster than the reaction can keep pace, and hence before the $FeCO_3$ of the interior is all decomposed, the other reactions of dehydration of the clay, and decarbonization of the other carbonates, are also taking place in the exterior of the mass. The CO_2 from $CaCO_3$ in particular is known to lag behind most other gases in the clay, and it is not wholly disengaged until the very time when the vitrification changes are apt to begin. This mineral therefore greatly complicates the oxidation of the iron salts on this account.

The outpouring of the steam and CO_2 from these minerals now fills the pores system of the clay. The pressure is within, struggling to get out. Hence, there is added to the mechanical difficulty of air penetrating the clay, the distinct current of other gases coming out under pressure. Naturally, therefore, oxidation is hindered until these reactions are complete.

Influence of Combustion Gases. It has been shown that FeO is prone to oxidize, even at ordinary atmospheric temperatures, when freely exposed to the air. But in the kiln, the atmosphere is no longer pure air. It is composed primarily of combustion products. The reaction of oxidation takes place, we may assume, between 400 and 900° C. It is most likely to occur between 700 and 900° C., because of the influences pointed out above. Supposing that no heat is being withdrawn for pyro-chemical processes in the wares, and that only the losses due to the escaping gases and the radiation of the kiln itself are to be accounted for, it is plain that to maintain a strong flow of gases through the kiln at a temperature of from 700 to 900° C. would require the steady consumption of a large quantity of fuel. Few people realize that the most rapid fuel consumption in the

whole burn is at just this period, and not at the end of the process, when the temperature is highest.

But if fuel must be burnt, then the air passing through must be laden with its products of combustion. If a fuel is burnt perfectly, and without excess air, its combustion products would be CO_2, H_2O, and N. If the air be in excess, O and more N are added to the mixture. If the combustion be imperfect, as it nearly always is, then the gases may contain in addition CO, CH_4, C_2H_4, CS_2, SO_2, NH_3, and H. These latter gases are all reducing in effect, and hence their effect on the process under discussion is strongly deterrent. It is remarkable that reducing gases and free oxygen may thus coexist, but analyses have repeatedly shown that such is the case.

The active value of the kiln gases for oxidising purposes depends, therefore, on several factors. 1st. The percentage of oxygen in the gases, 2nd the freedom from counteracting reducing gases, 3rd, the temperature. This field has not yet been fully studied, but the researches of T. Lowthian Bell in iron smelting have shown that Fe_2O_3 cannot be successfully reduced by furnace gas composed of CO, CO_2, and N, unless the ratio of the carbonic oxide to the carbonic acid has a certain value. The converse should be true in our case, viz., that FeO cannot be oxidized unless the ratio of the oxygen to the sum of the CO CO_2 and N has a certain value.

The lesson to be gained is, that mere exposure of clayware to the hot gases of a kiln, between 700 and 900°, while it must in time have an oxidizing effect, is by no means certain to rapidly perform the needed operation. It depends on how these gases are managed. If the fireman is acquainted with the objects of his work, he can so regulate his fires and his draft as to give his gases the utmost oxidizing value possible without loss of temperature. If he has no conception of these theoretical ends in view, he will probably make his fires work so that their gases are well nigh useless for oxidation purposes.

During the dehydration period, at least during the bulk of it, oxygen is plenty. Calculation shows that the waste

gases of the fuel must be diluted eight or ten volumes to reduce their dew point to a safe level during the drying off of a kiln. As the temperate rises, this enormous air excess decreases, but still may be three or four times what is needed for burning the fuel. But as soon as the ware is red hot through and through, the usual maxim of burners is to "push the fire as fast as the kiln will take it." They close the doors, or fill up the necks of the fire holes, and restrict the air supply, just at the very time when it is most needed.

Of course, it is evident that the air excess must be reduced, to permit the temperature to increase; but oxidation temperatures (700 to 900°) can be maintained with a very considerable air excess, if this point is duly understood by the burner, and made the subject of his skill and care.

In bad cases, when clays do not oxidize under ordinary treatment, a special procedure may be necessary to get round this difficulty. The Fish Brick Company, at Columbus, Ohio, use a bituminous pyritiferous shale, making a rather coarse-grained brick by the dry-press process, which they burn in the continuous kiln. They never have the least trouble from defective oxidation under these circumstances. But they made a few kilns by the plastic process, burning them in periodic kilns. They found, after considerable loss, that the following procedure was necessary.

The kiln was raised as usual up to about 900°C; the fires were then allowed to gradually die down to beds of ashes. The draft was reduced to a low point, and the kiln allowed to stand until the temperature had gradually fallen to 600°C, or nearly black. This took 12 to 18 hours. Then, firing up again, the kiln was carried up steadily to a finish. The secret of success in this case was the *long exposure to air nearly free from carbonic acid.* Eighteen hours of nearly pure hot air was effective, where three or four days of ordinary oxidizing at red heat had failed entirely to get the FeO all converted. Burners generally have a superstition to the effect that it is fatal to ware to allow the heat to drop back after once raising it to redness. There are good reasons in some cases, why this should be avoided. But in dealing

with such a case as this, it is practically the only way to get good results.

Deterrent Effect of Solid Reducing Agents in the Clay.

As has already been shown, clays very commonly contain organic and combustible matter. It is even added largely in many clayworking processes. Further, FeS is one of the common sources of iron in clays. These substances are all eager for oxygen and are stronger in their affinities than FeO is, Consequently, it is clear that no oxidation of the latter can possibly occur, while the former remain unoxidized.

Carbon is a constant source of trouble from this cause. Where sawdust or coaldust is plentifully added to a clay, even a well oxidized surface clay, it is quite often the case that reduction of the iron follows, and the clay shows black in the center after firing, just as if it had been a ferrous clay to start with. Still more, when a clay contains its carbon intimately disseminated through it, is it likely to prevent the oxidation of the ferrous oxide. The long and painstaking oxidation required to completely rid some clays of their carbon has already been illustrated in Fig. 3.

Sulphur is a still more troublesome substance, from the fact of its combination with iron, and consequent slowness to yield to roasting. FeS remains in black slag-like masses after the first molecule of S is expelled, and can only be destroyed by persistent and strong oxidation. Meanwhile, the iron cannot be effected, until the sulphur has been driven out.

The Effect of Structure of the Ware.

In the four preceding headings have been named the influences which are at work in the oxidation period of the burn. It is by no means to be supposed that in every clay, all of these influences are operating. In the typical brick and tile clays in use, no trouble is usually encountered, for the iron is already in the form of ferric hydroxide when it enters the kiln. Further, the clay is ordinarily sandy and open grained, and contains no sulphur and but little carbon.

Where the clay is an ordinary ferrous carbonate shale, the process is much more critical, but is still easily mastered. The hindrance to oxidation requires longer heating before vitrification, and also opener firing while raising heat. But the burner soon learns this trick, and no trouble need occur afterwards. The oxidation is here much affected by the structure of the ware. Shales ordinarily are not so very plastic. Therefore, when tempered up with water, they develop an open porous structure, favorable to oxidation.

The finer grained the clay, the more difficult does oxidation become. The writer has occasionally tested very fat, immensely fine grained clays, which do not show any grit between the teeth. Such clays will fail to oxidize and will bloat in firing, where other clays with three times as much ferrous iron will behave normally.

The fineness of grain therefore, becomes a factor of the greatest importance, and leads to practical steps to counteract its influence. Stoneware makers and sewer pipe makers have begun to find out that where they wish to make an unusually heavy piece of ware, that it is essential to open up the body of their clay by use of grog, The grog is prejudicial from one standpoint, but its aid in getting oxygen into the center of the thick ware in the same period of time as needed to reach the center of the ungrogged ware in thinner cross sections, more than over balances the detriment.

Also, brick makers have occasionally observed that an end-cut structure greatly hinders the oxidation. In one kiln made by the writer, containing about equal proportions of side-cuts and end-cuts from the same clay, the end-cuts were nearly all defective in the center and none of the side-cuts were affected. The difference comes in from the direction of the laminations, which make the center of one brick protected by sheath after sheath of clay, like a jelly roll, while the center of the side-cut is made accessible by the lamination leading into it.

Also the dry-press process and the plastic process offer some curious comparisons. In general, the latter structure is much the denser and harder to oxydize. But occasionally, a clay is encountered which is very soft and fine grained and

which packs in the dry-press die into a body of surpassing density. Such a body is exceedingly hard to oxidize, and can be worked much more safely in plastic form. But if in addition to having its iron in ferrous form, a clay contains carbonate of lime or magnesia, or pyrites, or carbon compounds, then trouble must be anticipated. The more of these materials the worse, and when all three are present together, the difficulties rise to the point of prohibiting economical manufacture.

Probably no clay exists, which *cannot* be burned safely. If it comes down to a struggle between a well equipped clayworker, and the natural perversities and disabilities of a clay, the clayworker can succeed, every time. But when the cost has to be considered, the difference between a low fuel bill and a high one; between a quick circuit of the kilns and a slow one; between a small percentage of loss and a high one; it is easy to see that some clays are better left alone. The writer knows of one instance where eighteen days were regularly required to burn a small round down-draft kiln of brick, where an ordinary Coal-measure shale should have been burned in seven. The trouble was carbon and sulphur and difficulty in securing oxidation.

Physical Structure of Clay at the End of the Oxidation Period.

The physical condition of the ware at the conclusion of the oxidation period is worth attention. If the work has been correctly done, the ware will be uniform in color in its whole cross section. Its color will be redder than at dehydration, if a red burning clay is used, or yellower if a buff clay is used. Its hardness will have sensibly increased, but it will still be soft. Shrinkage will have begun, but will have made but little headway. Strength will still be small.

On the other hand, if the clay be improperly oxidized, it will show on its fracture a spot, furthest from the exterior, of different color from the exterior of the ware. This new color is dark. The size of the spot will depend on the completeness or incompleteness of the work. The larger it is, the more certain it is to ruin the ware subsequently.

Fig. 3 very nicely shows this feature. The location of the spot will depend on the shape or position of the ware in the kiln.

In Fig. 4, the first piece on the left shows a brickette, with only a narrow border oxidized. The whole interior is untouched. But, the oxidation has penetrated about equally from all four sides. The second brickette shows the same process further along. The third brickette shows an unoxidized spot close to the left side. In this case, the brickette lay close to another, and the air got between the two with difficulty. In consequence, the protected side lagged behind the rest of the brickette.

It often happens that when bricks are faced or piled up closely on each other, that the exterior of the pile will oxidize, and the interior will not. This causes the brick to assume a fantastic appearance afterwards, one part being good and another bad, without the reason appearing from observation of the brick, apart from its setting.

In all that has been said so far, the allusions to trouble ensuing from incomplete oxidation have been frequent, but little has been said in explanation of what these troubles are. The reason for this reticence is that the real development of the trouble occurs only in the vitrification process. If the burn ended at 1000°C, then all of this discussion would be valueless. But hidden away in this apparently unimportant dark-colored spot are half the potential sources of trouble to which clays are heir; only when the vitrification of the ware is nearly finished, does this malevolent disease break out and show its capacity for damage.

THE VITRIFICATION PERIOD.

The period beginning about 900 B. C., represents the first constructive work in the burning process. All that has gone before is destructive of the original minerals which composed the clay, but not directly constructive of the homogeneous silicate, toward which the finished material is supposed to approximate.

To set forth the processes of vitrification in full detail, even if they were known, would be a task entirely beyond the scope of this present article. As a matter of fact, they are only dimly understood. The work of the cement chemists, the slag studies of the metallurgists, the work in lithological analysis by the mineralogists, all have given us something in this field, but a persevering study of the subject from the view point of the ceramist has yet to be made.

To understand the behavior of the iron in the processes which follow, we must have a little preliminary idea of the process itself. In brief, it is a continually changing series of combinations, in which more and more of the ingredients of the clay are drawn in.

The first change is thought to be a sort of condensation or shrinkage in itself of the kaolinite base of the clay. This precedes silicate formation, at least for the most part. Then the caustic basic oxides, lime and magnesia, begin to react on the dehydrated clay, forming silicates and aluminates. These soon give way to other compounds which bring the finest of the free quartz into combination. The feldspathic fluxes also begin to work, and thus from one combination to another, the work proceeds, building up one compound only to form another from it as the temperature increases and the materials present become more fully available.

If we stop the process at a number of different stages, take samples, and examine them critically, the physical structure is a warrant for the above outline. When cross sectioned and viewed under the microscope, the general truth of the above is proven, for crystalls of entirely different minerals can be identified in the same clay at different stages of its combination, and even in different parts of the same mass, where the heat has been uneven. These investigations have so far gone but a little way and the minerals formed in vitrifying clays have not yet been identified or described. We are far behind the cement chemists in this, for they have identified several minerals in portland cement

clinker, which is a much more difficult material to work with than ours, on account of its unstability.

The behavior of iron in the above process is the theme to which we must confine ourselves.

Phenomena Occurring at or before Complete Vitrification.

Vitrification among clay workers is a technical term. It does not mean, as many seem to think, that the clay has become converted into an absolutely homogeneous or glass-like solid, from which every vestige of the original mineral structure is obliterated. Such a condition is impossible in practical clay working. Even fusion does not accomplish go great a homogeneity, for when a clay is fused to a slag, its coarser particles have usually resisted solution and are still to be seen in the fluid magma.

To the practical clayworker, especially he who manufactures paving-brick, sewer-pipe, roofing tile, encaustic floor tile, stoneware pottery or porcelain, complete vitrification means that stage of a clay's burn where it becomes densest and strongest.

All clays pass in burning through a series of stages, and are progressively harder, stronger and denser up to a maximum; after that they begin to fall off, sometimes rapidly, sometimes slowly, until they finally become a worthless, vesicular, slag-like mass, devoid of useful qualities. The culminating point of excellence, though hard to define, is not hard to recognize. And while it does not by any means stand for the same qualities in any two clays, it is clearly defined to the practical man in dealing with each clay by itself.

For convenience, Wheeler* has divided the vitrification period into five stages, which mark well known differences in structure, though of course each stage passes insensibly into the next, without any dividing line. The four last stages he has named Incipient Vitrification, Complete Vitrification, Viscous Vitrification and Fusion. He gave no name to the first stage, but the writer has called it the Condensation period, as indicating that the chemical changes

* Vitrified Paving Brick, by H. A. Wheeler. Pub. Indianapolis, 1896.

occurring there are largely the simple condensation or shrinkage of the kaolinite, and perhaps other minerals, without involving actual silicate formation. Wheeler describes this stage as that of the ordinary well-burned red building-brick, which can be cut freely with a knife, and yet has shrunk considerably since dehydration.

The point of complete vitrification makes an excellent place to divide our discussion, for the reason that no one voluntarily passes it in producing clay wares. And, those changes which mature before or by that time are all familiar ones, which must be reckoned with daily. The changes which follow are destructive changes, to be avoided if possible.

The separate iron phenomena which occur before or by complete vitrification may be listed as follows:—

1st Development of the normal ferric color, red or buff.
2nd Development of the normal ferrous color, by reduction.
3rd Development of the abnormal black core, by faulty oxidation.
4th Blue-stoning, or the normal change from ferric to ferrous by increase of temperature under oxidizing conditions.
5th Reoxidation or flashing.

Development of the Normal Ferric Color. A red-burning clay which has been properly treated in the burn up to 900° C has acquired by that time a yellowish red, or pale-red color, which is called salmon. As the temperature continues to rise this color deepens and brightens, until by 1100° C, in most clays it attains its maximum brilliance and power. This red color is said to be that of free ferric oxide, which covers the grains of the other minerals with a film and creates almost as much color and as bright a tint as if the mass were ferric oxide throughout. Seger explains the successive shades of red by the increasing density of the iron oxide as the temperature rises. Condensation involves darkening of color, he argues, and cites experiments conducted on pure ferric oxide to prove the point.

The evidence that proves this to be the free ferric oxide

and not a ferric silicate, or aluminate, is more negative than positive however. It can be proven that the iron is in the ferric condition, readily enough. But to prove that it is not in combination, is not so easy. Solution of the iron is no longer possible to any agents except such as attack the rest of the clay as well. We judge by the color, which is ferric, and by the abrupt change in color which happens later on when silicate formation unquestionably does take place, that this red is that of the free oxide.

The question now arises, why is it that ferric oxide can remain so long out of combination, when surrounded by clay, silica, and other fluxing minerals, which are one by one breaking down and entering into bonds with one another? The question must remain unanswered. But experience proves that whatever the red color is, it remains intact for a long time as the heat rises, suffering no change except a gradual brightening and deepening in tint, up to a certain maximum. This maximum is not a fixed point for all clays. It varies with the composition of each. Those clays which keep it the longest are those containing least clay substance and most pure sand. A very sandy clay from Wisconsin was fired by the writer to cone 8 in a not very oxidizing burn, and remained a fine strong red, bordering on purple at this temperature. An ordinary red clay, containing 50 per cent. clay substance cannot be fired above cone 1 without beginning to show a decline. Soft fluxes like lead or alkalies, which promote silicate formation, tend to bring the iron into combination also, and destroy the red color of ferric oxide.

As a rule, the retention of the red color in its perfection and the development of a close, dense, glass-like vitrification seem to be mutually antipathetic conditions. That is, in most red-burning clays, their behavior seems clearly to bear out the contention that the color is due to *free* iron. For, as fast as the vitrification becomes visibly more perfect, the color darkens and the body seems to approach to its point of breaking down.

But occasionally, or rarely, a clay is met which contradicts this impression. Such clays have in the writers ex-

perience attained a vitrification almost like glass, preserving the while a red as bright and beautiful as sealing wax. Ink placed on the fracture, will dry and scale off without leaving a mark.

It is truly hard to see how iron can be wholly free and unattached in a silicate mass of such perfection. But, when such a clay is heated past this culminating point, it follows the general law, and blackens as it breaks down, thus seeming to show that combination of the iron means loss of its ferric character.

In one instance only, in an experience covering a large number of clays, has the writer found one which maintains a red color after passing into the vesicular stage of fusion. This clay is remarkable for immense fineness of grain, vitrification at extraordinarily low temperatures, and very early swelling into a spongy mass. It is possible that the exception is apparent rather than real, and that the clay really did blacken in fusing, but that owing to its spongy structure, and the low temperature and consequent excess of oxygen in the kiln gases, that *it reoxidized after blackening*. A supply of the clay has been secured for further tests.

A resume of the evidence, then, seems to indicate that clays are colored red by free ferric oxide, and that combination of iron with clay or silica involves blackening and formation of the *ferrous* silicate. The ferrous state of the iron in a black over-burned clay is easily proven by analysis. If this theory is not true, then the red color must be due to an unstable ferric silicate, which forms a stable black ferrous silicate after a certain critical temperature is reached. Most clays seem to favor the former hypothesis. A very few favor to the latter. It must be borne in mind, however, that these latter clays all vitrify very early, and before the ordinary range of temperatures are reached. No instance of a clay has yet come to the writer's attention which burns to a vitreous red at a high temperature.

The behavior of buff-burning clays runs parallel to the above described phenomena, except that there is much less difference between the soft and fully matured ware than be-

tween salmon and good red. The latter change is almost a change in kind, while the former is one of degree. Also, during the retention of the buff color, complete or glassy vitrification is not quite so uncommon as the sealing-wax red. But, aside from the fundamental difference in the color, the two series pass through about the same course of events, and bear out the same conclusions.

Development of Normal Ferrous Color, by Reduction. One of the strong arguments for a free ferric oxide as the basis of the red or buff color, is the prompt destruction of that color by anything like reduction. Reducing gases, smoky fire, dirty grates, or restricted air supply, very soon produce a greenish or bluish black coloration in a red or buff ware. This blue-black material is readily proved to be ferrous by analytical means. To prove that it is a silicate is not so easy. But, proceeding on synthetic lines, we can make ferrous silicates by fusion, and they all have a black color, comparable directly with that obtained in the reduced clay. When we attempt to produce a ferric silicate of a red color, if exclude the solution of Fe_2O_3 in a gloss or glaze, we fail.

The rapidity of the change from red to black depends upon (a) the violence of the reducing condition and (b) the porosity of the ware, by which the gas reaches the ferric oxide or ferric compound. Open spongy structures are affected almost at once. Dense vitrified structures suffer gradual change; sometimes several hours of continuous reduction will still fail to penetrate the center of a mass.

This reaction is exceedingly common among producers of vitrified wares. If the reduction occurred late in the burn, during the flashing or salt glazing process, it very frequently shows as a blue-black ring, extending in an eighth or a quarter of an inch from the surface, and surrounding a bright red core. Sewer pipes especially are prone to exhibit this phase, owing to the sharp pushing of the fires during the salt glazing, which is itself a reducing reaction.

Figure 5 shows several samples of this change. The piece on the left is a sidewalk paver, which has been reduced from a yellowish buff to a blue black, on one side and

FIG. 5. SEE PAGE 416.

FIG. 6. SEE PAGE 418.

edge especially. The other surfaces were somewhat protected. The next piece is from a buff sewer-pipe. The interior surface shows the heaviest reduction, and the exterior surface shows a lighter, but distinct black ring. The next two pieces are parts of hollow building block, made from a clay which burns pale red. The blue-black color has proceeded half way through the piece. The piece on the right is a paving brick, of which only about one third still retains its bright red color. The blackening has gone in nearly an inch from every surface.

The permanence of such a reaction depends on the degree of vitrification attained. If the ware be porous, the reduction is ephemeral, being replaced by oxidation with equal ease. In short, while porous, the colors may be made to fluctuate with each firing, if the burner wishes. But, as the ware gains in vitrification and becomes impervious to gas flow, the colors become slower to create and slower to replace.

The effects of this reaction on the strength and value of the ware are not good. The black ferrous silicate does not seem to be as strong or durable a body as the red ferric compound. Paving brick which are thus blue-skinned, or smoked, usually wear badly for a time at least, the black crust breaking off in brittle spalls, showing the red beneath like an open wound. When shale pavers first began to be used, city engineers frequently went far beyond their province in specifying the exact color which they would require a brick to be, and many brick makers learned to put a blue exterior in a red brick to meet just this kind of demand. The results were bad and the practice has now been generally discontinued. Enough of such brick are produced by accident, without having recourse to intention.

In wares like sewer pipe, however, which have no wear to endure, this change in color and loss of strength are much less prejudicial. But, if the black color be produced, another form of the same reaction is very likely to also take place, which *is* very prejudicial indeed. I refer to the formation of bubbles, pimples, eruptions etc. on the surface of the wares.

Sewer pipe and conduit makers have no more troublesome defects to overcome than this bubbling. Paving brick makers suffer less, but face brick makers, especially those making flashed bricks, are very subject to it. No one likes to see an otherwise smooth clay product covered with little pimples or ragged-edged blisters of black slag.

The cause of this slag is the same as that of the blue-black coloration. It comes however from the occurrence of the iron in the form of concretionary grains. These masses of iron, while they remain ferric, will not readily combine with the clay. The writer has seen a case where grains of iron were still unfused in a buff face-brick burned at cone 8. The firing was done with natural gas, and the kiln atmosphere was perfectly oxidizing throughout the burn. The clay had blue stoned, but the iron had not slagged in the least.

But, let the atmosphere become reducing and these grains rapidly change to ferrous oxide. This oxide readily unites with silica or clay substance, and the result is speedily a little pool of a basic iron silicate. It is too basic to be very fluid, or to let gases escape from it or through it, so it becomes inflated and forms a little bubble. If the heat continues to rise, these in time melt, become fully fluid and finally lie flat and smooth on the surface as black velvety spots. But, if the bubble be formed at the maximum temperature of the kiln, then on cooling the wares are covered with these unsightly eruptions.

Fig. 6 shows a very bad case of this reaction on a flashed brick. The iron was excessive in amount, excessively large in grain, and the cooling happened at just the right time to show this reaction at its very worst. It is on that account instructive.

The remedy for this condition is to avoid reduction at the end of the burn. If the fires are kept clear, the grates kept clean, a certain amount of air admitted over the top of the fire, and no heavy black smoke created in firing, this pimpling on the surface, where due to iron, will not occur. With some fuels it is very difficult to avoid reduction; the choice of a proper fire place and the training of the burners

to fire frequently and but little at a time, is the remedy in such cases.

Development of the Abnormal Black Color, by Faulty Oxidation. This reaction is not to be construed as different from the preceding in so far as the actual chemical process, or the character of the black silicate itself is concerned. The reason for its description under a separate heading is merely to emphasize the causes leading up to its development, and to aid clayworkers in recognizing the phenomenon when they see it. It has already been stated that failure to bring the clay to perfect oxidation at the lower range of temperatures, 600 to 1000°C, before vitrification sets in, is one of the most destructive errors commonly made in the burning of ceramic products. It is so troublesome, because it is so insidious. No external evidence of the trouble is shown till too late. The process of burning goes along without a hitch, until the finish is close at hand, and then it suddenly shows. But then, it is long past help.

There are two reasons why a clayware which is not oxidized at the proper time is never oxidized: First, the porosity of the ware rapidly diminishes as the temperature rises. Some clays mature wonderfully quickly in the temperature range between 1000° and 1100°. The majority of red-burning glacial and alluvial clays mature in this short range. Others, the shales and the sandier common clays, require another 100° to bring them to maturity, and, consequently, still continue to oxidize with fair ease long after the close-bodied, easily-vitrified clays are past the limit.

Second. The composition of the fire gases becomes less and less fit to oxidize the ferrous oxide as the temperature increases. It has been already pointed out that free oxygen *in large excess* is necessary to rapid oxidation. But as the temperature of the kiln increases, the products of combustion will stand less and less dilution with free air without becoming too cool. As the temperature reaches 1200°, it becomes practically impossible to admit any excess air, or rather, the combustion fluctuates between oxidizing and reducing with each baiting of coal, so that the average gas produced is neu-

tral. Where temperature of cone 8 or above is used, the reducing reaction predominates.

Where for any special ware it is essential to maintain oxidizing conditions to a high temperature, 1300° or above, it is necessary either to so construct the firebox and bags as to obtain a regenerative effect on the air supply, and thus decrease its cooling effect, or to use gas fuel or some similar device. With cold air and solid fuel it is very difficult, if not impossible, to prevent occasional reduction at even 1200° C.

On these two accounts, there is but little probability of the clay oxidizing after 1000° C. is reached. In fact, but little of account happens after 900° C. Hence, for all practical purposes, we may say that when ware is not oxidized at the right time, it will not be oxidized at all.

Having now established the primary cause of the defect, let us consider its mode of operation. The central fact in this connection is that ferrous oxide combines with silica and clay at temperatures far lower than ferric oxide does. Without at this time discussing the final breaking down of a red-burning clay by excess of heat, we know that if fully oxidized and red throughout, it will stand a temperature far above that at which the black ferrous structure forms and becomes semi-fluid. It is this difference in melting point which causes all the trouble. If it did not exist, then the condition of the iron would be immaterial.

Nor is the mere fact of fusion in itself so very disastrous. The final and most troublesome fact in the whole series is the evolution of gases by the ferrous slag. It is a matter of common observation, that silicates nearly always undergo a scoriaceous stage in fusion. In glass melting this is well marked, and in order to avoid its effects the temperature of the glass is run up till it becomes very fluid indeed. After a proper exposure to this temperature, the gas evolution gradually ceases and the glass settles back into a clear, dense fluid.

The same general facts may be observed in slag fusions, or in any other silicate fusion. Clay silicates are no exception. When they melt, there is every likelihood of a considerable evolution of gases, and these swell the ware up into spongy, slaglike masses, sometimes actually so light as to

float on water. The only difference between clay and the silicates is that in the latter we aim to produce fusion, and push it far enough to get rid of the gases, but in clay we never aim to produce fusion, and consequently only carry our heating up to the very edge of this stage. Hence we encounter the very beginning of the gas evolution. In a few cases, the writer has seen clays fused completely into solid glasses, free from gas bubbles, but it is rarely that the overheating is sufficient to produce this state.

The gases which are evolved are not definitely known. There are but few which can be counted as possibilities. 1st, CO_2, from carbonates, especially carbonate of calcium, or from the gradual oxidation of carbon still inclosed in the mass. 2d, SO_2 or SO_3, from the breaking down of sulphites or sulphates, or the gradual oxidation of sulphide of iron still enclosed in the mass. 3d, H_2O, if any could still be present as part of a hydrous compound or a hydrocarbon not thoroughly coked. The latter seems improbable.

The amount of gas evolution is a variable factor. It depends on the following conditions: 1st, the amount of material in the original clay which is capable of producing gas, *i. e.*, the amount of carbon, carbonates and sulphides; 2d, the completeness with which these substances have been burned out from the clay while it was still porous; 3d, the amount of overheating after the gases begin to come off. The worst clays to deal with are those which contain carbon, carbonates, sulphides and iron, all together. Such a composition is a fatal handicap to profitable manufacture. But it must be remembered that the actual volume of the gases set free may be a very trifling amount, and still be capable of working a great injury to the ware. The gases, as soon as they are set free, expand with each increase in temperature and become worse in their effects thereby.

The time of the gas evolution depends somewhat on the clay itself. Beyond a doubt, every silicate has its own formation temperature, and before this is reached, it is innocuous. These clay silicates have not yet been studied so carefully as to enable us to say anything on this head. But, the sili-

cate formed will depend on the composition of the clay, and it is quite likely that several silicates form and dissolve one in the other, producing a slag whose melting point as a whole is referable to no single silicate. Thus a clay of fine grain and high in fluxes may blacken and swell very much earlier than another of coarse grain and low in fluxes. But in both, the same general relation between the blackening of the ferrous core, and the breaking down of the oxidized exterior seems to prevail. That is, the red oxidized portion of one clay may break down from excess of heat, before the black core of another clay may begin to swell, showing that black coring is a phenomenon which is consistent with its own clay, but not comparable, clay with clay. In general, the defect becomes evident just prior to the normal finishing of the kiln. The red portion of the ware is usually approaching its best strength when the black portion becomes so scoriaceous as to attract attention by the change in shape

Allusion has been made incidentally in many places in the foregoing pages to the effects of this gas evolution. In brief, they involve a swelling or bloating of the black ferrous portion, and a sufficient stretching of the surrounding red portion to accommodate the change in volume. Naturally the extent of this bloating depends on the amount of gas liberated, the increase in temperature after liberation, and the structure of the red portion of the body. If the latter is porous, the swelling will be slight or unnoticeable. If it is dense and impervious, the swelling will be very severe. The action is exactly that of yeast in a loaf of bread, except that it proceeds from a central focus instead of throughout the structure equally..

The practical range which this troublesome defect may take in claywares is very great. Figure 7 shows two bricks split longitudinally, illustrating a very bad case of deformation. The red ferric shell is about one-half inch in thickness on the sides, thicker on the ends and corners. The black spongy core has generated such a volume of gas that it has created large cavities between it and the exterior. These bricks were made from a carbonaceous, pyritiferous, ferrous

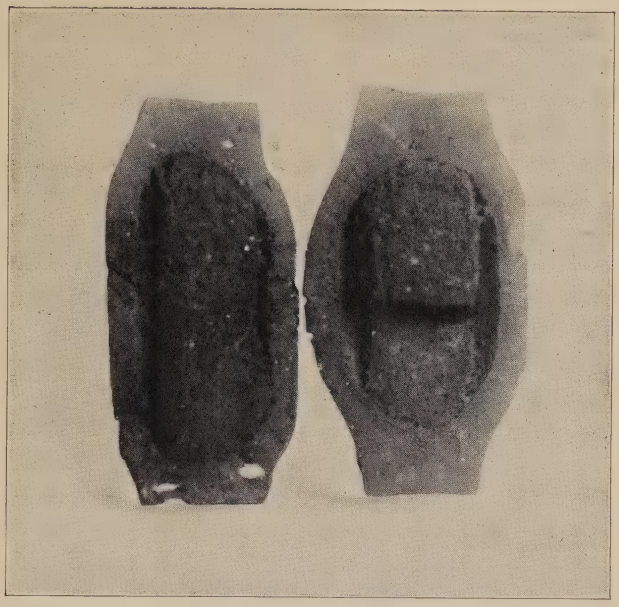


FIG. 7. SEE PAGE 422.

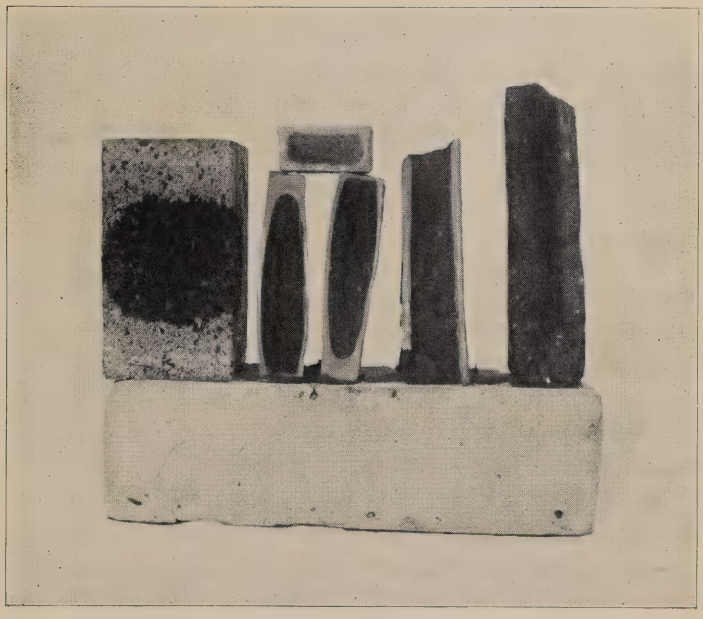


FIG. 8. SEE PAGE 423.

shale, by the stiff-mud process. Even this does not represent the maximum. Cases have come under observation where the clay has bloated up to three or four times its original volume.

A more moderate phase of the defect is shown in Fig. 8. On the right is a piece of red sewer pipe. The blue core is here about one-third of the cross section, and the gas evolution has been small. Consequently, the ware is not swollen; but it is weak and brittle. There seems to be a very distinct difference between the physical properties of the blue and red, because the ware is invariably weakened by a blue core, even when the vesicular structure is microscopic. This constitutes one of its chief disadvantages; swollen wares can be picked out and discarded. But when they are merely blue-cored, their unsoundness only develops by use. After the failure has come, we see why it came. But that does not guard against its recurrence.

The piece next the right is a beautiful example of change in color, without swelling. It is from a drain tile, made of a tough fine-grained alluvial clay, which would ordinarily speaking be called perfectly safe from such defects. The piece was burned in about 24 hours, which explains the trouble. The two small pieces next the left, are trial pieces burnt by students. They show the contrast in a buff clay very prettily, and also show slight swelling. On top of them, is another small trial piece, in which only a faint blue core shows—no swelling. The brick on the left shows a dry-press product, made from a fire-clay containing some carbon. It has not swollen, but the brick was so weak as to be rejected from use. In other instances, this defect may represent merely a faint blue line or spot in the thickest and best protected portion in the ware. In such cases, its power to do harm is small.

Summarizing, we may say that failure to oxidize the clay to the center at the proper time, usually results in the failure to oxidize later. The ferrous oxide thus left forms a fusible silicate at a temperature when the well oxidized exterior is only becoming well vitrified. This fusible silicate evolves gases, in greater or less volume, which tend to swell the

ware. In cases where the amount of fusible silicate is small or the gases are not abundant, the discolored core does not swell, but weakens the product by unequal expansion and contraction.

Blue Stoneing, or the Normal Change in Color by Increase in Temperature. With this phenomenon, every clayworker and many ordinary observers outside of the clay industry are familiar. With its cause, few if any can claim knowledge. The writer acknowledges that it has gone no farther than speculation with him.

The brick shown in the bottom row in Fig. 9 are red burning paving brick. All are thoroughly vitrified in the usual sense that clayworkers use this term. None of them would absorb more than a fraction of a per cent. of water. But the left hand one is red as liver, the middle one is a dark red, almost a chocolate, and the third is of a purple or violet color. In the upper row, on the left, is a buff fire-clay brick; next, the same changed to a soft blue-gray tint, and on the right a darker purple-gray. None of the six samples are in the least swollen or vesicular. None are reduced by gases working on the interior or exterior. They have simply changed color by increase of temperature, being maintained all the while in oxidizing conditions.

It is easily possible to overburn either of these clays, but in the ordinary acceptation of this word, these clays are not overburned. Their strength and hardness and density are about uniform throughout the series. A small increase of temperature would bring an abrupt and marked physical change in both of the right hand specimens, which will be described later on.

What, then, is this mysterious change in color. The writer believes it is the preliminary stage of that breaking down by which the ferric oxide, or ferric compound, whatever it may be, is converted into ferrous oxide by the superior energy of the silica and formed into a ferrous silicate. This reaction, if there is such a one, is brought into full completion during fusion, and its further discussion will be deferred till that topic is reached.

The alternative proposition to which we are driven is

FIG. 9. SEE PAGE 424.

that advanced by Seger, who thinks that the increasing density of the ferric oxide as the temperature mounts higher, is sufficient to explain all these shades between light red or buff and violet black. He does admit that ferric and ferrous oxide, in different proportions, may cause a wonderful variety of tints. No one would oppose this statement. But, the question arises, how could a densely vitrified mass of clay like a brick, being heated in purely oxidizing atmosphere, generate any such mysterious mixture of ferrous and ferric oxide, after it has once safely passed the oxidizing period?

Whatever its cause, all clays show this phenomenon to a greater or less degree. Sometimes, as in the limy clays, the transition from vitrification to fusion is very short. But in its traverse, however short or long it may be, this mysterious, delicate change of color comes. It must not be confounded with any of the oxidation or reduction phenomena discussed heretofore.

Reoxidation, or Flashing. This topic has already been discussed by Bleininger and others, and will therefore receive but a word here. It has been shown that where a clay is frequently subjected to alternate oxidizing and reducing conditions, that it shows a change in color, which is superficial if the ware is vitrified and dense, and entire when the ware is porous. This color is that produced by ferric oxide, only darker and stronger. In a buff clay, it is golden, russet or brown. In a red clay, it is chocolate or almost black.

It has been shown that this color, cannot be developed by a continuously oxidizing burn. It requires reduction, *followed by oxidation*, to develop it. The more times this change occurs, the more brilliant the color and the easier it is to develop. It also requires that the reoxidation shall be as well marked as the reduction. A cooling under reducing conditions, or a very short or sudden cooling, leaves the ware in its reduced or ferrous color.

These facts are now well in hand and of commercial use among the numerous class of clayworkers who are producing flashed brick, and similar wares. I propose to dwell for a moment on another phase of the subject which is never pro-

duced with intention, which is counted a defect, and which is generally not comprehended by those who encounter it.

The two bricks shown in Fig. 10, were made for buff bricks. But in the center of one, and on the side of the other, is a zone of distinctly pinkish color, quite widely different from the clear cream color of the rest of the ware. These pink spots were reduced in the burn, but not by gases and under the burner's control, as in flashing. They were reduced by the carbon in the clay itself, which was in a way fixed or "set" in the clay by too sudden heating. It is not unlike the way that a dye sets in a fabric under the influence of a mordant.

Carbon, especially that of the bituminous type, is very difficult to handle. It is apt to catch fire, and raise the heat too fast. Or it is likely to decompose, or "crack," and deposit a fine coke in every pore of the clay, where it can only be burnt out with the extremest care and plenty of time. But, by slow firing, by cutting off the air supply, by use of grog or grit in the body, and similar means, this may be overcome or avoided.

If carbon is once allowed to remain in the clay till a good red heat is reached, then its effect is inevitable. It will reduce the iron. If this be carefully reoxidized the black core may be obviated. But, the reoxidized iron will no longer take the same color, as the exterior shell. It takes the redder, stronger tint instead. Thousands of face brick go for seconds every year on account of this defect, which could be avoided by a little more care or a little more understanding of this simple fact.

Phenomena Occurring after Vitrification or by Reason of Excessive Heat.

The natural end of the heating process is fusion. But clayworkers only push their process to this extreme by accident. In the very large majority of cases, the substance produced by the fusion of the clay as a whole, is distinctly refractory. That is, it does not melt readily, compared to slags, glasses, and other artificial silicates. On this account,

clays generally pass from vitrification into fusion by slow and insensible stages. This quality is very necessary to satisfactory clay-burning. Where the temperature interval is short, as in the limey clays, they become very "unsafe," *i. e.*, the burner must pay the penalty of the least excess of heat, with a lot of fused and worthless ware.

The stage known as viscous vitrification is the form of overburning shown in the great majority of cases. The limits of this state are defined, first, by the point where the clayware is no longer able to resist the pressures which it has to endure under normal kiln conditions; second, when the ware is unable to endure its own weight and sinks out of shape by gravitation alone.

In dealing with different products the setting is managed on so widely different plans that normal kiln pressures are not comparable. A paving brick carrying the weight of thirty superincumbent courses is certain to sink out of shape far earlier than a piece of pottery in a saggar. Therefore viscous vitrification does not mean the same stage of fluidity in different products.

In no clay do the whole mass of the minerals arrive at fusion simultaneously. In vitrification we must conceive of a mass or skeleton of rigid unfused minerals greatly in preponderance, permeated by a small proportion of fused silicate matter. This latter is enough to tie the other materials together, to render the mass harder and stronger, but not to cause it to lose its shape. But, as the process goes on, the proportions of stiff rigid matter and fused matter are gradually reversed. The point at which a ware yields to kiln pressure and deforms, therefore, depends (*a*) on the proportion of coarse-grained relatively infusible, insoluble minerals which will act as the skeleton or frame to resist change of shape; (*b*) on the kind of a solvent fluid slag which is attacking this skeleton and undermining its power to resist; (*c*) on the pressure or weight to which the ware is subjected.

The nature of the breaking-down process has been discussed already, in connection with black coring and bluestoning. The exact nature of the chemical compounds which fuse first, and thus lead to a fusion of the clay as a

whole, are not known. It is not likely that they are the same in many cases. Or, rather, that the total number of minerals which may form in a fusing clay is large, but that the proportions of each in any given case are not likely to be duplicated by any other case. It is probably a case of solution of one silicate in another, and in many cases we are not likely to resolve the question of proportion in the near future or by existing means.

There are two facts in connection with the breaking down of a clay by heat which are noteworthy, viz., the developement of the vescicular structure, by gas evolution, and the change of color. These two phenomena are not invariably manifested, but only in very rare instances do they fail. The clays which fuse most quietly are white-burning bodies using lime as a flux. The writer does not recall a red- or buff burning clay which fused without gas evolution.

The explanations given of gas evolution in the formation of the ferrous silicate at lower temperatures hold good here only in part. The chief difference is in the quantity and nature of the gas-forming substances still left in the clay. Water and probably CO_2 are now ruled out. The clay having been thoroughly oxidized and thoroughly vitrified, is supposed to contain nothing further combustible or readily volatile. There are two other sources of gas remaining; first, SO_3, from the breaking down of sulphates, which are known to resist decomposition much more tenaciously than carbonates or any other salts found in clays; second, oxygen, derived from the breaking down of Fe_2O_3 to $2FeO$, before passing into silicate combination.

The Vesicular Structure Produced by Sulphates. Beyond a doubt, this swelling is a common and important cause of the breaking down of clays. In Fig. 11 are shown two cases. The fireclay brick has become minutely cellular, and has increased in all dimensions about equally. Fusion has not set in; viscous vitrification is admirably represented. But the brick has lost its hardness, strength and density to a considerable extent. Its color has not materially changed. This seems a typical case of sulphuric acid swelling.

The red brick is a dry-pressed ware made from a pyrit-

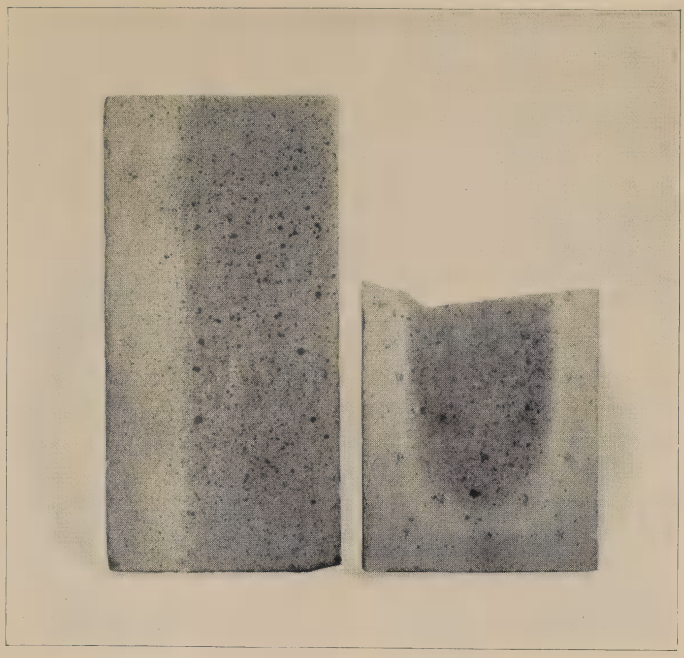


FIG. 10 SEE PAGE 426.

FIG. 11. SEE PAGE 428.

eferous clay. It has swollen much more, and less regularly than the other. It is fused, rather than in the stage of viscous vitrification. It also has lost strength, hardness and density. Its color has changed somewhat, *but is still red.* The entire absence of darkening in the center proves that the clay has been fully oxidized. Moreover, its heating has been but little above the point of complete vitrification. The other end of the same brick was sound. This also seems a clear case of sulphuric acid swelling.

The Oxygen Hypothesis. The two cases above have been picked out as unusual. Ordinary claywares blacken extensively in fusion. And their swelling occurs with and in proportion to their blackening. This seems a significant fact. While red or buff, analysis demonstrates their iron to be ferric. But after this breaking down and blackening, it shows it to be ferrous. This change has occurred progressively from outside to inside, as the temperature is taken up from the gases surrounding the ware.

It is hardly possible to explain this sudden change by reduction by gases, which we know operates so frequently at lower temperatures. This might happen slowly and gradually, if the gases were persistently kept reducing. But how could these gases penetrate a dense vitrified structure and reduce its iron in a few minutes? And yet a few minutes of overheating is enough to cause the change.

The writer has long held the opinion that this change in color and in structure has its explanation in the breaking down of the ferric oxide, into ferrous oxide, with evolution of oxygen. This theory accords with all observed facts, so far as they are at hand; its sole weakness is the hypothetical breaking down of the Fe_2O_3 without the aid of a reducing agent. This has seemed improbable to many to whom it has been suggested. But there are many other instances of oxides breaking down by heat alone. If this hypothesis is ultimately proved to be true, it only adds another oxide to the list.

It will lead too far to discuss the whole question of the existance of ferric silicate at this point. But we know at least, that ferrous silicates are easily made synthetically and

that ordinary technical and industrial work does not offer similar illustrations of ferric silicates. The breaking down of the iron under stress of high temperature, and the action of silica in immediately forming the black silicate, seems to more adequately explain the observed facts than any other theory yet advanced.

In the preceding pages, the writer has marshalled the principal facts concerning the behavior of iron in clay burning as they have appeared to him. In closing, he wishes to repeat the opening remarks, to the effect that there is much more of opinion than research in the paper. If it suffices to show the very numerous gaps in our exact knowledge of this important and fascinating subject, and inspires in the mind of any the desire to unravel any one of these problems, it will have answered its purpose well.

NOTE BY THE SECRETARY.

The foregoing paper was delivered at the Boston meeting in the form of an address. Since that time, it has been extended and considerably changed in method of presentation. In view of these changes, it has been thought best not to print the discussion which occurred after the address, but to specially request those who spoke at that time to formulate their views in detail and send them in in writing for publication at a later time.